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SOIL INTERACTION WITH ORGANICALLY POLLUTED WATER

J. W. Biggar, et al

California University
Davis, California

February 1966

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SOIL INTERACTION WITH ORGANICALLY POLLUTED WATER

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Department of Water Science and Engineering
University of California
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SOIL INTERACTION WITH ORGANICALLY POLLUTED WATER

By
J. W. Biggar, L. D. Doneen and R. R. Riggs

February 1966

Summary Report

Prepared Under
Research Grant No. WP-00081
Division of Water Supply and Pollution Control
Public Health Service
Department of Health, Education and Welfare

ABSTRACT-SUMMARY

The fate of pesticides in soils and water depends upon the solubility in water of the material, diffusion, characteristics, adsorptive or exchange properties with respect to the soil or solid matrix, convective movement and other organic material. To some degree these characteristics will also affect the degradation of the material although this is not a part of the present investigation.

The solubility in water of p,p'-DDT as well as a number of other chlorinated hydrocarbons has been investigated. The low solubility of DDT in water is believed to be a major factor in minimizing degradation, diffusive movement and movement by mass flow of water regardless of the adsorption. The preparative treatment of DDT prior to analysis was shown to affect the concentration in solutions.

One factor of particular importance that is often overlooked is the relation of temperature to the solubility of the pesticide in water. For a range of 15°C to 45°C the concentration of pesticide in water may change by 2 to 8 times. Included in these temperature solubility studies were Lindane, DDT, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide and Nemagon (1, 2-dibrome -3-chloro propane). Solubility of the pesticide in water is a prerequisite for further studies of the adsorption and movement of the materials in water.

Apparent self diffusion coefficients of p,p'-DDT and related breakdown products measured in Na Kaolinite substantiated the conclusion that solubility was an important factor in movement. This particular factor is expected to be more significant than the type of cation or soil material involved. These latter points are yet to be studied. If a solubilizing agent is present, the diffusion coefficient of DDT is of the same order as adsorbed cations, e.g., 10^{-6} to 10^{-7} cm^2/sec.

Flow studies conducted in apparatus capable of maintaining constant pressure and water content conditions illustrated the mixing that takes place when DDT emulsions flow through soils. A mixture of 50% ethyl alcohol and 50% water containing 50 ppm p,p'-DDT displaced $CaSO_4$ water and

was in turn displaced from Oakley sand soil. The breakthrough and elution curves illustrate the adsorption that occurs, the contribution of diffusion to the mixing, the mixing by velocity variations and the significant movement of DDT when an emulsifier of this type is present. Again the solubility is a significant factor in the movement. Further studies to be reported later, are presently being conducted in columns of various length, with varying alcohol to water ratios and velocities.

Adsorption studies of p,p'-DDT on Na, Ca bentonites and Kaolinite illustrate the role the solvent plays in controlling the uptake of an adsorbate by these materials. No completely satisfactory model for the adsorption of DDT by these materials was formulated since the data was somewhat erratic. For purposes of describing the adsorption during transport through soils however, the Langmuir model is being tested. Considerable difficulty has been experienced in obtaining satisfactory adsorption data on soils. This difficulty appears to have been solved by using radioactive isotopes in preliminary studies. The method will be checked with gas chromatography to guard against decomposition products which yield misleading interpretation as illustrated by diffusion studies.

ACKNOWLEDGEMENTS

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INTRODUCTION

1.1 General Problem

The movement of pesticides, herbicides and other materials in and over the soil may contribute significantly to the pollution of surface and ground water supplies. Major carrier of these materials is water, although both aerosols and natural soil erosion contribute to the transport of these organic materials.

In most applications, investigators have been mainly concerned with the effectiveness of pesticides in performing a particular function. Whether the materials are fixed, leached, or degraded has been regarded as important only insofar as these reactions affect their usefulness in pest control; the potential pollution and toxicity of decomposition products was rarely considered. As a result, necessary information linking the reactions between pesticide and soil, and pesticide and plants, to the characteristics of each other, the soil solution environment, temperature and water movement is very spotty and incomplete. This is the status of current work in this area and suggested the need for a project to obtain a reasonable amount of related information on fixation and movement for typical soil materials and selected pesticides.

The use of pesticides in agriculture is not new. However, the quantities and types of these materials have greatly increased in recent years. Intensive public interest, by reason of concern for public health, has arisen with respect to the fate of these materials both in soil and water. The demonstrated presence of pesticides in streams (2, 13, 14, 16, 22) and the associations of their presence to fish and wildlife kills has clearly implicated agricultural users. Most evidence is circumstantial, however, with little to indicate that appreciable pollution results when pesticides are properly used.

1.2 Review of Literature

Bailey and White (1) have recently reviewed the current literature available on a wide variety of herbicides, fungicides, insecticides and their interaction with soil and other materials.

It is evident from the literature that soil texture, organic matter, time of contact, temperature, moisture, as well as soil solution characteristics, affect the leaching of pesticides. Getzin and Chapman (5) working with five systemic insecticides and sand, silt loam, clay loam and muck found reduced activity with increasing fineness of texture and increasing organic matter content. Hanks (6) studied six soils with a wide range in pH and physical properties. He added lime to some samples and treated the soils with 2, 4-D acid and its Ca salt. After leaching with 10 and 16 inches of water over a 6-week period all soils leached with 16 inches were free of toxicity indicating removal of 2, 4-D. Lime produced no significant differences in leaching of the material. Minarik (15) tested the leachability of the Ca, Mg, K, Na, and NH_4 salts of 2, 4-D and found them to be more soluble than the acid form or salts of Fe and Cu. An association between solubility and leachability was evident. Smith and Ennis (18), contrary to Minarik (15) observed no differences in the movement of salts of 2, 4-D. Upchurch et al. (21) investigated the leaching of monuron from soil columns of Lakeland sand. Over a temperature range of 5 to 40°C. the monuron retained below the 2-inch depth increased with temperature. As the organic matter increased from 0.87 to 1.44% the amount of monuron retained increased from 35 to 95%. Moisture content at application time had little influence on monuron retention.

Gargantini et al. (4) studied the leaching of BHC in blocks of sandy soil. After 6 months and 1079 mm. of water 90% of the BHC was retained in the top 10 mm. and 0.4% in the bottom layer. Swanson et al. (20) leached lindane (BHC) through various soils using ether. Retention of lindane increased as the clay content and the exchangeable Mg increased. Adsorption rather than exchange is postulated as the retention mechanisms. Lichtenstein et al. (10) studied the vertical distribution of aldrin and heptachlor incorporated into the soil in the field. Of the residue recovered a year after application, 90% was found near the surface; deeper penetration was indicated 3 years later. Increased residues under alfalfa versus fallow plots indicates the reduction in water movement under cropping conditions. The same author (11) investigated the leaching of aldrin, lindane and DDT from a silt

loam and muck soil after incorporation in field lots. A loam soil retained 84 to 96% of these insecticides in the upper 3 inches after 17 months. The fact that twice as much insecticide was found at the bottom of gently sloping plots indicates transport of the insecticides by surface water movement or soil erosion, to be a possible source of contamination of return flow water. Muck soil retained more lindane and parathion than sandy soil in leaching experiments.

Since the adsorption, exchange and degradation of the pesticide in soils can prevent leaching of the original applied material (not necessarily its degradation products), it is necessary to know the occurrence and nature of the reactions in order to predict the extent of leaching which may occur. Weidhaas et al. (23) found that C^{14}-DDT and P^{32}-parathion were strongly adsorbed by soil from aqueous solutions. After 24 hours, 50 g. of soil absorbed 78% of the DDT and lesser amounts of parathion from 100 to 200 ml. of solution containing 0.02 p.p.m. of the insecticide.

Hanson et al. (7) reported that sorption of EDB strongly depended upon the water content. Diffusion of the material also depended upon the porosity, temperature and moisture content. Jurinak and Volman (9) found the BET equation described the adsorption of EDB on very dry soils at 24.6°C. up to relative pressures of 0.6. Adsorption appeared to occur only on external surfaces. The heat adsorption of EDB was 700 to 1100 calories per mole greater on montmorillonitic soils than kaolinitic or illitic soils.

Frissel et al. (3) examined the interaction of several herbicides with clay minerals. The organic compounds included acids and weak bases. Adsorption isotherms revealed that the main variables of concern were pH and electrolyte concentration of the system. The observed reactions were discussed in terms of coulombic and non-coulombic interactions between the organic additive and soil. Prediction of adsorption under field conditions based on equilibrium laboratory measurements were made by the authors.

Little mention has been made in the above review concerning methods of analysis. Many investigations have depended upon biological assays for detection of the additive or for an estimate of its activity. These methods may be adequate for evaluation of the material in the control of a pest but they are not sufficiently sensitive for quantitative studies of leaching or reactions with soils. New and more sensitive methods of detection have been described (8, 12, 13); much development work on methods of detection and identification is currently in progress at several centers.

The references cited concerning the presence and reactions of agricultural chemicals in soil and water do not exhaust the list of publications that could be included. The review has emphasized insecticides because of their obvious importance to food chains and to public health but the case is the same for herbicides and other pesticide chemicals. The main point to be made is that few investigations have not been concerned with the problem outlined in this proposal, the contamination of water by agricultural chemicals. More quantitative information is clearly needed concerning the presence and nature of these materials in surface water. The source and method of transport is required in some cases. For pesticides there is a lack of information on the energetics of their reactions with the soil. Where information exists, there is no link between the adsorption and movement or leaching. The biological destruction and subsequent removal of by-products of many materials has been seriously neglected. A coordinated program to obtain a reasonable amount of related information is essential in order to establish the source of agricultural contaminants, the nature of their movement and reactions in soil, and management practices suitable to the performance of their function without undue contamination of water supplies. This information is required for efficient and safe management of chemicals in the production of quality foods and to safeguard public health.

1.3 Objectives:

To determine the equilibrium relationships between chlorinated hydrocarbons and other selected organic additives with selected clay types and soils. The effect of adsorbed cations and inorganic salts in the equilibrium solution upon the reactions of organic additives with these materials was to be included in the investigation. Studies on molecular diffusion of the additive in clay systems and other porous material were to be conducted. The interactions of adsorption and diffusion were to be considered. In the subsequent studies, this was accomplished by considering flow systems as well as diffusion experiments.

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SECTION I. Solubility of p,p'-DDT by gas chromatography

2.1 Introduction

In the course of developing techniques for studying the adsorption and movement in soil of extremely dilute aqueous p,p'-DDT suspensions, it was essential to determine the solubility of p,p'-DDT in water under identical experimental conditions to those experienced in adsorption and movement studies. Furthermore, it seemed desirable to determine whether the concentration of DDT in a stable suspension could be predicted by thermodynamic considerations for a set of conditions different from those examined experimentally.

The literature contains several values for the solubility of DDT obtained by a variety of analytical techniques. Richards and Cuthomp (7) reported a range of 0.2 to 1.0 ppb at 15°C determined by bioassay with mosquito larvae while Roeder and Weiant (8) estimated 10 to 100 ppb at room temperature as determined by nerve reactions in cockroaches. Babers (2) and Bowman et al. (3) reported values of 37.4 ppb and 1.2 ppb at 25°C respectively, determined by radiometric analysis. Gauvadan and Poussel (5) estimated a solubility of 100 ppb at 18°C by a nephelometric technique.

In addition to being highly sensitive to halogenated hydrocarbons, electron capture detectors together with appropriate chromatography columns afford an accurate method of analysis of the purity of a compound. This eliminates the error introduced by soluble impurities in the radiometric method. Problems associated with codistillation, surface phase concentration changes, and particle size distribution have been previously mentioned (3). The use of the centrifuge in obtaining a particular particle size can be analyzed thermodynamically. However, it is not possible to establish from solubility measurements alone what the importance of DDT particle size distribution is to transport through porous material. Such considerations are under investigation elsewhere. Nevertheless it is essential to establish reliable means of analysis capable of detecting DDT in aqueous solutions which do not depend upon radiometry because of DDT in surface and ground water supplies as well

as soils (4, 9, 10). DDT in water supplies and the means of deposition there must be related to solubility measurements by additional experiments to be reported later. In the present paper analytical methods are described as well as solubility determinations and predictions of solubility based on thermodynamic equations.

2.2 Theory

The system to be considered is

$$DDT_{(l)} \rightleftarrows DDT_{(s)} \qquad [1]$$

where (s) refers to solid phase p,p'-DDT and (l) refers to p,p'-DDT in solution. The chemical potential μ of DDT can be written as

$$\mu_I = \mu_I^{\circ} + RT \ln a_{(s)} - RT \ln a_{(l)} \qquad [2]$$

where μ_I° is the chemical potential in the reference state in a gravity field of unity; $a_{(l)}$ and $a_{(s)}$ are the activities in the solution and solid states respectively. By definition $a_{(s)} = 1.0$ for the solid phase and since at equilibrium $\Delta\bar{G} = \mu_I = 0$ equation (2) becomes

$$\mu^{\circ}_I = RT \ln a_1 \qquad [3]$$

where $\bar{G}$ is the partial molar free energy. When the system is subjected to an external field such as that which occurs in a centrifuge in motion then the chemical potential μ and the partial molar free energy are not equivalent. An additional term must be added to the chemical potential to account for the increase in energy of the constituents as a result of the external field (6). Normally this is neglected for ions and in the case of DDT in the unit gravity field has been included in the reference state. We wish to compare the concentration in the solution after centrifugation with the concentration in the reference state of unit gravity.

For the centrifuged samples

$$G = \mu + \frac{1}{2} m v^2 \qquad [4]$$

where G is the free energy, m the mass and v the linear velocity of the rotor.

Since

$$m = n_1 M_1 + n_2 M_2 + \ldots\ldots \qquad [5]$$

where n_1 is the number of moles of constituent 1 and M_1 the molecular weight, then

$$\left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2} + \ldots = \bar{G}_1 = \mu_1 + \frac{1}{2} v^2 \left(\frac{\partial m}{\partial n_1}\right)_{P,T,n_2} \ldots \qquad [6]$$

$$\bar{G}_1 = \mu_1 + \frac{1}{2} M_1 v^2 \qquad [7]$$

For two different positions in the centrifugal field at constant temperature and pressure at equilibrium

$$\bar{G}_a - \bar{G}_b = \left(\mu + \frac{1}{2} M v^2\right)_a - \left(\mu + \frac{1}{2} M v^2\right)_b \qquad [8]$$

where the subscripts a and b refer to two positions in the field.

Since $\bar{G}_a = \bar{G}_b$ at equilibrium and

$$\mu = \mu^\circ + RT \ln a$$

$$0 = RT \ln a_a - RT \ln a_b + \frac{1}{2} M (v_a^2 - v_b^2) \qquad [9]$$

$$RT \ln a_b/a_a = \frac{1}{2} M (v_a^2 - v_b^2)$$

For these dilute solutions the activity coefficient is assumed to be 1.0, and taking the activity equal to the concentration, equation (9) becomes

$$RT \ln C_b/C_a = (v_b^2 - v_a^2) \frac{1}{2} M (v_a^2 - v_b^2) \qquad [10]$$

where C_b refers to the solution concentration at 1.0 G ($v_b = 0$), and C_a the concentration at some velocity v_a in the centrifugal field.

2.3 Experimental

Preparation of Aqueous Suspensions. Pure p,p'-DDT (99.9%) was prepared from an original sample of 99.3% purity by repeated recrystallization from absolute methanol until a single chromatographic peak with no detectable decomposition was obtained. An acetone solution of p,p'-DDT was prepared, and an appropriate quantity was transferred to a glass-stoppered flask. Water, double distilled from glass, was added to the flask. In this manner, suspensions of 25 ppb DDT were prepared. The suspension was heated on a steam bath and shaken for one hour, then shaken for 6 days at 25°C in a constant temperature bath. The suspension was then filtered through a sintered glass filter funnel of 5 micron porosity. The filtrate was collected in a glass-stoppered flask and stored at 25°C until sampled or analyzed.

Method of Sampling. The filtrate was shaken immediately prior to each sampling to ensure uniform dispersion. Stainless steel centrifuge tubes (seven groups of four tubes) were filled to contain 50 ml. of filtrate each, and were capped to prevent loss during centrifuging. The tubes were centrifuged at 25°C $\pm$ 1°C for periods of 6, 12, 18, and 24 hours, at speeds of 5000 and subsequently 18000 r.p.m., in a Sorvall RC-2 centrifuge. At the end of each centrifuging, the top half of the filtrate was withdrawn from each tube by pipette and combined with others of the same group. The pipette was rinsed with redistilled n-hexane, the rinse being added to the sample, which was extracted once with 50 ml. of n-hexane, then twice further extracted with 25 ml. aliquots. The extracts were combined, concentrated to 1 ml. and chromatographed. Additional dilutions or concentrations were made when necessary to obtain a linear detector response.

Method of Analysis. The gas chromatographic analyses were performed on an Aerograph Model A-600-B gas chromatograph equipped with a 250 mc tritium-foil concentric tube electron capture detector, operated at a potential of 90 volts. The 5' x 1/8" pyrex column was packed with 5% Dow 11 on 60/80 mesh Chromosorb W. Water-pumped nitrogen was the carrier gas, at a flow rate of 100 ml/min. The column oven temperature was 180°C isothermal. The injector and detector were

maintained at 200°C. A pyrex injector insert was used to minimize decomposition. The 5µl samples were injected with a 701N CH Hamilton syringe. The detector signal was recorded at a sensitivity of X8 with a Brown Electronik 15 1 mv-1 sec. recorder equipped with a 201-B Disc Integrator.

2.4 Results and Discussion

The approximate solubility of p,p'-DDT was estimated from suspensions of technical DDT and 10 p.p.m. suspensions of p,p'-DDT. It was observed that the minor components (26.2%) of technical DDT (o,p'-DDT, o,o'-DDT, p,p'-TDE and p,p'-DDE) had a greater solubility in water than did the p,p'-DDT. This would account for the high values reported by Babers (2) and Bowman et al. (2). The o,p'-DDT, o,o'-DDT, and p,p'-TDE, and the dehydrohalogenation products of o,p'-DDT and p,p'-TDE, could not be resolved under the above conditions. Consequently the solubilities of the minor constituents were not further investigated.

The rate of adsorption of p,p'-DDT by stainless steel tubes was found to be less than that of any other centrifuge tube capable of withstanding the experimental conditions. It was found necessary to correct the data by subtracting the amount of DDT adsorbed on standing. Codistillation was avoided by employing closed systems. The efficiency of the liquid-liquid extraction procedure was 99-100%.

After preliminary work, the concentration of p,p'-DDT in suspension was reduced to 25 ppb. The filtrates of these suspensions contained 12.1 ppb.

Figure 1 presents the concentration of p,p'-DDT in the solution for various centrifuge speeds and times. It appears that after 24 hours an equilibrium has been established at 18000 rpm (39,100 G), 12000 (17,300 G) and 0.0 rpm (1 G). The corresponding concentrations are 1.7 $\pm$ 0.17 ppb, 2.0 ppb, and 3.4 $\pm$ 0.17 ppb. Substituting in equation (10) M = 354.5, R = 8.314 x 10^7, T = 298°K, at 18000 rpm, the ratio C_b/C_a = 2.1. Taking C_a = 1.7 ppb, C_b = 3.57 ppb which

compares with the measured value of 3.4 ppb. For similar conditions except the speed is now 12000 rpm, the ratio C_b/C_a = 1.54 and for C_a = 2.0, C_b = 3.1 ppb. The measured value is 3.4 ppb at 24 hours. Hence the measured values and calculated values are all within 10% of each other which is satisfactory at these low concentrations.

One set of samples that was centrifuged until the concentration remained at 1.7 ppb were set aside at constant temperature conditions and sampled at various times. The slow increase in concentration is illustrated in Figure 1 by the curve with the 10 x; note the different time scale. After 200 hours, the concentration had reached 3.0 ppb in the upper half of the tubes and it appeared to be approaching a value of approximately 3.4 ppb, the concentration approached from the other direction when the initial concentration was 9.5 ppb.

The value of 1.7 ppb obtained in this work is in close agreement with the value obtained by Bowman et al. (3) who used the radiometric method and higher centrifugal force. However, our purpose was not only to measure the solubility in water of DDT by this method, but to check the method against other determinations. This was desirable since other experimental work suggested the use of the E.C.G.L.C. method. It was also desirable to relate the concentration at some standardized centrifuged treatment to the concentration without centrifugation. This we are able to do.

In terms of the behavior of DDT in soils or streams it can be argued that the concentration of 3.4 ppb is more realistic than 1.7 ppb. This is true even though the concentration of DDT in waters often is less than 1 ppb. On the other hand, the low solubility of DDT in water may account for the fact that it is such a persistent pesticide, resistent to breakdown. This last point is to be investigated further.

The analysis of natural waters for pesticides by gas chromatography has been reported elsewhere (4, 9, 10) and need not be discussed here.

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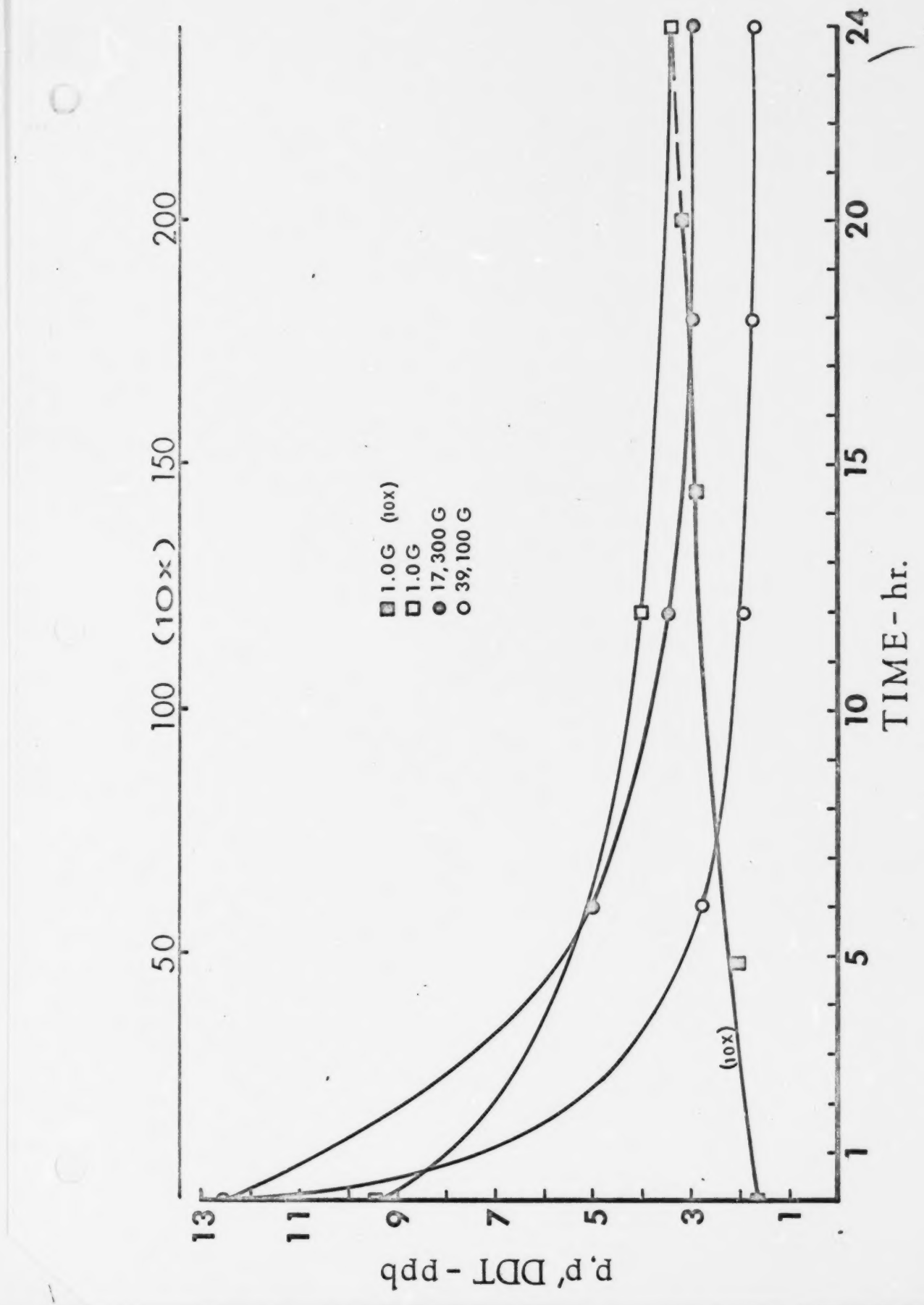
2.6 Figures

Figure 1. Changes in the concentration of p,p'-DDT in water with time for various treatments with and without centrifugation.


p,p' DDT - ppb
13
11
9
7
5
3
1
50
100 (10×)
150
200
1.0G (10x)
1.0G
17,300 G
39,100 G
(10x)
1
5
10
15
20
24
TIME - hr.

SECTION II. Solubility-Temperature Interactions of Selected Chlorinated Hydrocarbons

3.1 Introduction

In addition to the intensive studies that are being conducted on p,p'-DDT, certain other chlorinated hydrocarbons were to be selected for investigation. The time required to develop techniques for investigating these materials is considerably reduced as a result of experience gained with DDT investigations. Some of the difficulties of analysis are not as critical since the solubility of most other materials in water is much greater than DDT.

A survey of the literature soon revealed that no satisfactory data were available for the solubility in water of several of the materials of interest. Yet if one is to assess interactions and movement of pesticides in soils and waters, a prime prerequisite is a knowledge of the solubility of the materials in water. It is also recognized that many pesticides are used in a prepared form which makes them compatible with aqueous solutions. The use of emulsifiers and other agents can significantly modify many interactions. However, it is necessary and useful both for comparative as well as predictive purposes to know the solubility of the material themselves in water and how it is measured (see Section I). Examples of how an emulsifier can affect the transport of the pesticide are given in Sections III and IV. A second factor which is normally overlooked, particularly since many pesticides are highly soluble in water, is the effect of temperature on the solubility. This factor as we shall see, is particularly significant with respect to certain chlorinated hydrocarbons including the cyclodienes. It has special significance in relation to the concentrations of pesticide in different bodies of water.

3.2 Theory

Consider a system consisting of N_A^s moles of solid A, plus N_A^l moles of A dissolved in N_B^l moles of solvent. The free energy G of the system is

$$G = N_A^s \mu_A^s + N_A^l \mu_A^l + N_B^l \mu_B^l \qquad [1]$$

where μ is the chemical potential, l is liquid and s the solid phase. If a small quantity of solid dn is now dissolved the free energy will be

$$G + dG = (N_A^s - dn)\ \mu_A^s + (N_A^l + dn)\ \mu_A^l + N_B^l\ \mu^l{}_B$$

The change in free energy at constant temperature and pressure is

$$dG = (\mu_A^l - \mu_A^s)\ dn$$

or

$$\frac{dG}{dn} = \mu_A^l - \mu_A^s \qquad [2]$$

An approximate quantitative estimate of the variation with temperature of the solubility of a solid in a solvent in which it forms a perfect solution can be arrived at as follows:

$$\mu_A^s = \mu_A^l = \mu_A^{0,1} + RT\ \ln(X_A)_{Sat} \qquad [3]$$

where the standard state of A is identified with the pure supercooled (meta stable) liquid A. The solubility may be written as

$$\ln(X_A)_{Sat} = \frac{\mu_A^s - \mu_A^{0,1}}{RT} \qquad [4]$$

The chemical potential of pure solid A and pure supercooled liquid A may be written in terms of their molar heat contents and entropies,

$$\mu_A^s = h_A^s - T\ s_A^s \qquad [5]$$

$$\mu_A^{0,1} = h_A^{0,1} - T\, s_A^{0,1} \qquad [6]$$

so that

$$\mu_A^s - \mu_A^{0,1} = (h_A^s - h_A^{0,1}) - T\,(s_A^s - s_A^{0,1}) \qquad [7]$$

$$= -\,(\Delta_f h - T\Delta s_f) \qquad [8]$$

where h and s are the molar heat contents and entropies and T the absolute temperature.

At the melting point T_f of a solid

$$\Delta s_f = \frac{\Delta hf}{T_f} \qquad [9]$$

and assuming these are independent of temperature we may substitute for Δs_f to obtain

$$\mu_A^s - \mu_A^{0,1} = -\,\Delta h_f\,(1 - T/T_f) \qquad [10]$$

Substituting in equation (4) we have

$$\ln(X_A)_{Sat} = -\,\frac{\Delta h_f}{R}\,\left(\frac{1}{T} - \frac{1}{T_f}\right) \qquad [11]$$

The log of the solubility expressed in mole fractions is a linear function of 1/T. It should be recognized these relations hold only for ideal solutions and that systems under examination may only approximately fulfill the requirements. However, the relationships are useful over a limited temperature range for comparison of materials and their reactions in aqueous mixtures.

3.3 Method

To either 1 or 2 liters of distilled water, pesticides in an excess amount were added in the following concentrations: Lindane 20 ppm, Nemagon 1500 ppm, all others 5 ppm. Ultrasonic suspension (1) is a useful means of preparing such suspensions. The samples

were then shaken for 2 weeks in a constant temperature bath at 15, 25, 35 and 45°C ± 0.05°C. They were filtered through a sintered glass filter of 4-5-5.5μ porosity followed by centrifugation at the above temperatures for one half hour at 18000 rpm (equivalent particle size of 0.05μ). Aliquots of 100 and 200 ml. were taken after filtration and again after centrifuging the aliquots were three times extracted with n-hexane (redistilled over Na) using 100:50:50 ml. volumes. Extracts were combined, put through a column of Na_2SO_4 and concentrated to 10 ml. using Kuderna-Davich evaporative concentrators. One to five microliter aliquots of concentrate were chromatographed using a Wilkens Aerograph 600 B employing concentric 250 mcH^3 electron capture source operated at 90V. Other G.C. parameters were as follows:

Column: 5' x 118" pyrex; 5% Dow 11 on 60/80 Chromosorb W

Carrier Gas: Water pumped N_2 at 50 ml/min except as below

Column Temperature: 180°C

Injection Temperature: 225°C

Detector Temperature: 200°C

Flow rates for dieldrin, endrin, DDE were 100 ml/min

Attenuation: X8

Recorder 1 mv Honeywell at 1/2" per min

3.4 Results

Table I lists the concentrations in solution of the pesticides investigated at two particle sizes and 25°C.

Table I

Concentration in water of pesticide in ppb at 25°C as a function of equivalent particle size		
	0.05	5.0
Lindane	600	6800
Aldrin	140	180
Dieldrin	150	195
Endrin	180	250
Technical DDT (A)	15	35
Technical DDT (B)	17	40
o,p'-DDT		85
p,p'-DDE		120
p,p'-DDT	6	25
Heptachlor		180
Heptachlor epoxide		200
*Nemagon		1150 (ppm)

*Note Nemagon concentration in ppm.

As noted in Section I in the discussion of DDT, the treatment of the liquid prior to the analysis (e.g., filtering, centrifuging, etc.) can have a significant effect on the concentration in the liquid. This is more noticeable with lindane. and endrin. The concentrations of p,p'-DDT are higher than reported previously because of the shorter centrifuge time. However, for similar treatment it is noticed that o,p'-DDT, p,p'-DDE and the Technical DDT are all of greater solubility.

The effect of temperature is even more revealing and should not be overlooked when considering changes in pesticide concentration in rivers, lakes, ground waters and storage reservoirs. The data presented in Table II and Figure 1 of this section indicates that the quantity of pesticide in the liquid phase may be increased by 2 to 7

times when the temperature increases from 15 to 45°C. In Figure 1 a plot of the ln X, the concentrations in the liquid phase vs. 1/T as required by equation (11) is linear with some scattering of points. The reason for this seems evident and further experimentation is proceeding to check this point.

The related cyclodienes, dieldrin, aldrin, and endrin have a similar range of temperature - solubility interaction. There is sufficient difference in them however to warrant additional investigations related to adsorption and degradation.

Table II

Solubility of chlorinated Hydrocarbon Insecticides in water as a function of temperature. Particle size equivalent to 5.0 μ

		Temperature °C			
Compound	% Purity	15	25	35	45
Lindane	99+	2150	6800	11400	
Aldrin[1/]	99+	105	180	350	600
Dieldrin[1/]	99+	90	195	400	650
Endrin[1/]	99+	130	250	420	625
p,p'-DDT	99+	17	25	37	45
Technical DDT	*	23	40	55	

*76% p,p'-DDT; 22% o,p'-DDT; o,o'-DDT; p,p'-TDE; 2% p,p'-DDE.

1/ Solubilities in Hexane of aldrin, dieldrin, endrin are 98, 7.7 and 7.1 gm/100 ml. @ 25°C.

Additional studies of adsorption on clays and soils with temperature are anticipated in view of the significant changes in the solubility with time. Likewise temperature studies on desorption and movement in columns of soil are anticipated.

In summary it may be concluded that the affect of temperature on the solubility of these materials in water is much too important to be overlooked - particularly with respect to adsorption and degradation.

3.5 Literature Cited

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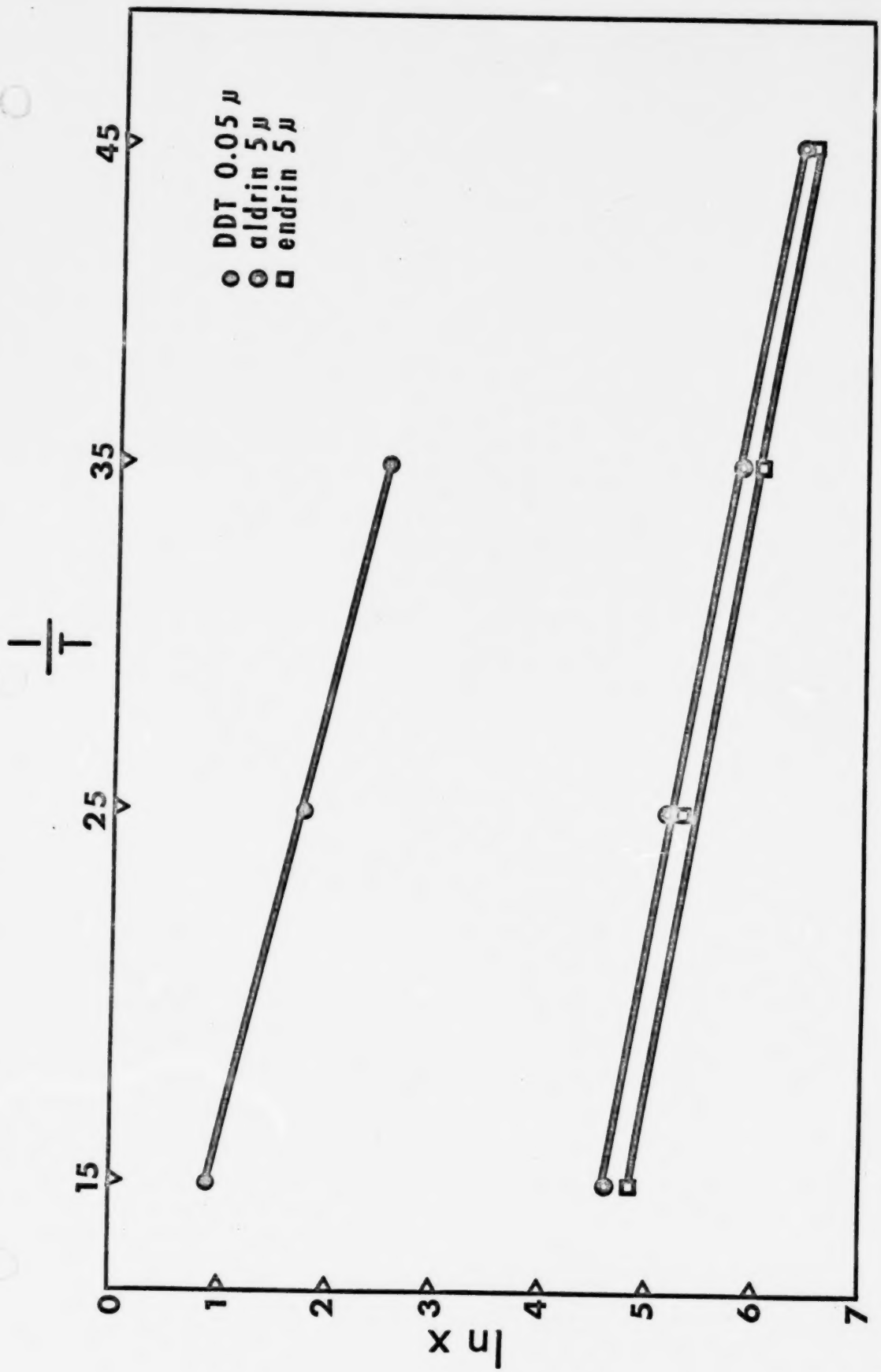
3.6 Figures

Figure 1. Solubility of pesticides as a function of the reciprocal temperature. Concentration of pesticide expressed in ppb instead of mole fraction.


DDT 0.05 µ
aldrin 5 µ
endrin 5 µ
1/T
15
25
35
45
ln x
0
1
2
3
4
5
6
7

SECTION III. Apparent Self-Diffusion Coefficients for p,p'-DDT in Clay

4.1 Introduction

One of the most significant processes in the transport and movement of ions and molecules in soil and soil solution is diffusion. The importance of the process is underscored by the extensive literature on the subject, both in systems in which mass flow of water is zero and in systems in which both flow and diffusion occur (1).

One of the particular objectives of the present investigation was to examine the diffusion of DDT in clays and soils. Diffusion coefficients for various cations have been measured by a number of methods. Husted and Low (4) measured self and counter-diffusion of Na and K in bentonite gels containing free salt solution. Lai and Mortland (5) examined the self and counter-diffusion of Li, Na, Cs, K and S in electrolyte-free bentonite gels using tagged salt solutions. Self-diffusion values of Na, Cs and Co in agar cores were measured by Thomas (9) using tagged ions and gels in contact with membranes and rapidly stirred solutions. Phillips and Brown (7) reported self-diffusion and counter-diffusion coefficients of Rb and H in soil, kaolinite and montmorillonite clays.

The two half cell radioisotope technique has been used in various designs to obtain diffusion coefficients. Schofield and Graham-Bryce (8) inserted an ion exchange resin disc between two half cells to study diffusion of Rb, Sr, I and P in soils. Gast (3) used a much more complicated stacking arrangement of half cells while Patil *et al*. (6) reported diffusion coefficients of Rb^{86} using two half cells, one tagged with Rb^{86} and the other untagged.

From the review of studies made, it was evident the measurements of inorganic ion diffusion in clays were much more extensive than organic ions or molecules. Furthermore, the diffusion of pesticide materials has been discussed more in connection with gaseous materials and no work appears to have been reported for the very slightly soluble chlorinated hydrocarbons.

After preliminary experiments the method of Brown et al. (2) was adopted with modifications in technique and procedure to handle the systems under study.

4.2 Materials and Methods

Samples of sodium saturated kaolinite were obtained from the large uniform batch prepared for studies on diffusion and adsorption described in Appendix I.

The clay (< 2μ size) was made homoionic and leached free of soluble salts. Soils and in particular Columbia silt loam were also prepared by making them homoionic and leaching free of salt for diffusion studies. Additional details are included in Appendix I.

Diffusion Units

Diffusion cells initially were constructed of lucite tubing 2 cm in length and 2 cm inside diameter. The cells were split into equal halves longitudinally. The halves of each cell were held firmly together by plastic tape so that the frozen clay plugs could easily be removed from the cells by removing the tape and lucite containers.

Lucite presses were made of the design similar to a hamburger patty press but of the proper dimensions to hold a diffusion cell firmly together when closed. These presses were used to maintain a constant reproducible pressure on the cells. The presses were 3x3x2 inches with cylindrical recessed parts to accommodate the cells.

The cells were uniformly packed with clay or soil, the one half-cell containing Cl^{36} DDT and the other component or half-cell with non-tagged DDT. Since the concentration added to the clays was the same for each half-cell, the diffusion process occurred as the self-diffusion of DDT. The clay protruded slightly from the back end of the cell in order to give a positive pressure at the interface. The outside ends of the core were covered with plastic plates to which the pressure was applied. The diffusion was allowed to occur for a specified length of time prior to freezing and sectioning.

After some initial investigations it was found desirable to study the diffusion of DDT in systems of decreasing dioxane and increasing water content. This was demanded by the low solubility of DDT in water and the difficulties of DDT analysis (at low concentrations) in clays. The test cells had to be modified to improve the freezing characteristics of the plugs and prevent liquid migration.

As a result, rectangular cells of 1/16" thick aluminum metal were formed, 1 3/16" long and 7/32" wide, split longitudinally. These were treated much the same as the plastic cells but had better thermal characteristics for the dioxane-water-DDT systems. In order to minimize the loss of more volatile solvents, it was found helpful to wax the units with paraffin prior to storage for the diffusion reaction.

Freezing and Sectioning Cores

The cells were maintained at 25°C ± 1°C during the diffusion reaction. At the end of 5 hours (time varies according to solvents), the cores were dipped in liquid nitrogen for 30 seconds. Longer or shorter times were necessary depending upon the dioxane-water mixture. Overfreezing caused cracking and underfreezing produced a deformable plug difficult to section.

After freezing, the core was removed from the cells and set on the pre-cooled sample head of a refrigerated microtome that was pre-cooled to -10 to -20°C. A few drops of distilled water froze the core to the sample stud. The core and holder were then stored in the microtome cabinet for sectioning for 0.5-1.0 hours.

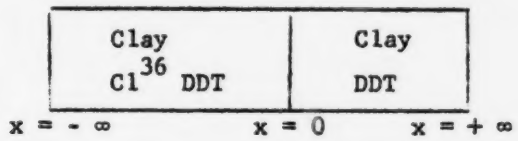
The freezing of the core has been shown (2) to reduce the diffusion significantly. For Rb^{86} the diffusion coefficient over a three-month period was found to be 3×10^{-10} $cm^2/sec.$ at -12°C in kaolinite clay.

The sectioning was accomplished by mounting the core in an International-Harris refrigerated cryostat containing an International rotary microtome, Model CT. The disposable blade was positioned to take a cut perpendicular to the axis of the plug and was set to cut 32 micron thick sections. The sections were caught in a pre-cooled spatula, pre-cooled to prevent sticking of the clay to the spatula.

Ten sections were collected and placed in a 1.0" diameter by 5/16" high stainless steel counting pan containing 2 ml of ethyl alcohol for dispersing the clay. Agitating the pan gave excellent distribution for drying and counting the clay. The alcohol was dried under low heat (< 50°C) and low air movement. The planchets were weighted and counted in a glass flow thin window counter. The radiation and weight data were then used to express the activity in terms of counts per minute per milligram of clay or soil. These data were used to prepare ion-distribution curves and to calculate the apparent diffusion coefficients.

4.3 Theory

The schematic diagram of the geometrics of the diffusion problem is given below.



The movement of ions is in the $\pm x$ direction (one direction only). Fick's second law is applicable as given in equation [1].

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad , \quad \begin{matrix} -\infty < x < +\infty \\ t \geq 0 \end{matrix} \qquad [1]$$

where C is concentration of ions per unit volume in the clay, D is the apparent diffusion coefficient, t is time, and x is distance. The initial conditions are given by equations [2] and [3], see Gast (3).

$$C(x_1 o) = C_o \quad , \quad -\infty < x < o \qquad [2]$$

$$C(x_1 o) = 0 \quad , \quad o < x - +\infty \qquad [3]$$

The total ions Q_1 remaining in the clay in the region $-1 < x < o$ at the same time is

$$Q_1 = AC_o 1 - Q = AC_o 1 - AC_o (Dt/\pi)^{\frac{1}{2}}$$

where $AC_o l$ represents the ions present in the region $-l < x < o$ at time $t = o$. With $Q/(Q + Q_1) = F$ and rearranging, an expression for D the apparent self-diffusion coefficient is obtained.

$$D = \frac{\pi l^2 F^2}{t}$$

where the reference frame is the entire clay sample.

The length of the clay medium extends to $x = \pm \infty$ and the concentration of ions C remains constant at $x = \pm \infty$ for all times. The solution of [1] for conditions [2] and [3] is

$$C(x_1 t) = C_o/2 \left[1 - \text{erf } x/2(Dt)^{\frac{1}{2}}\right] \qquad [4]$$

For a medium of finite length where $x = \pm 1$, equation 4 is valid providing

$C(-1, t) = C_o$ and

$C(+1, t) = 0$ where

t is the time allowed for diffusion.

Then the total quantity of ions Q which have diffused from $-l < x < o$ across the boundary $x = o$ in time t is given as

$$Q = DA \int_o^t \frac{\partial c(o,t)}{\partial x}\, dt$$

$$= AC_o \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

where A is the cross sectional area of the diffusion cell containing the clay or soil.

4.4 Results and Discussion

In the work reported here considerable time has been concentrated on the sodium kaolinite system for perfecting techniques and obtaining representative data for one chlorinated hydrocarbon p,p'DDT. Because of the extremely low solubility of p,p'DDT in water (see Section I), it was found desirable to study the diffusion process in dioxane-water mixtures ranging from 100% dioxane to 10% dioxane. By this method quantitative data could be obtained to estimate the diffusion coefficient of DDT in water. This approach to the problem has the additional advantage of establishing ranges of diffusion coefficients for systems in which the DDT is solubilized by an emulsifier and therefore is more mobile.

Kaolinite-Dioxane-Water System

Sodium kaolinite clay (< 2μ), salt free, was mixed with an equal weight of dioxane or dioxane-water mixtures to give 100% liquid content. Parapara DDT in concentrations of 250, 50, 10, 1 ppm was added to the clay either with Cl^{36} tagged DDT or without the radioisotope. The total concentration of DDT was the same in each half all with sufficient isotope percent to allow radioanalysis. The diffusion was allowed to occur for 5 hours at 25°C ± 0.5°C before sectioning.

The results obtained in Section IV concerning adsorption indicate that the clay will adsorb some of the added DDT. The amount of DDT in solution will also be related to the ratio of dioxane to water liquid content. DDT is more soluble in dioxane than water.

An excess of DDT was added to the systems such that more DDT is present in the system than will be adsorbed from solution. Experiments indicate that the diffusion coefficients were the same within experimental error of 10 percent whether the DDT added was 250 ppm, 50 ppm, or 10 ppm. However, the accuracy of the data is improved if an excessive amount of radioisotope is avoided. Hence the data presented in figures 1, 2, 3, and 4 represent additions of 50 ppm of DDT.

Figures 1, 2, 3, and 4 present data for systems of decreasing dioxane and increasing water in the liquid mixture. The circles are

experimental data and the solid lines theoretical curves according to equation [4] with the values of the apparent diffusion coefficients given in Table I.

Table I - Apparent self-diffusion coefficients, D, cm^2 per sec., of Cl^{36} p,p'DDT in sodium kaolinite for various percentages of dioxane-water mixtures at 25°C.

% Dioxane	% Water	D
100	--	3.1×10^{-6}
75	25	2.1×10^{-6}
50	50	1.34×10^{-7}
25	75	2.1×10^{-8}
--	100 *	1.0×10^{-5} *

* Diffusion coefficient for Cl^{36} in Na kaolinite with NaCl as the salt in solution.

The limited solubility of p,p'DDT in water (1.7 ppb - 3.4 ppb, Section I) clearly manifests itself in this table. As the water content increases, the quantity of mobile DDT decreases and is precipitated or adsorbed on the clay surfaces. In effect, it is trapped by the presence of a liquid in which it does not dissolve and therefore must remain on the surface.

For purposes of comparison the apparent diffusion coefficient for Cl^{36} in the same Na kaolinite at the same water content but for a NaCl, $NaCl^{36}$ system is presented in Table I. It is evident, even under conditions of favorable solubility that p,p'DDT has a D one order of magnitude less than the inorganic ion and this decreases with increasing water content.

Figure 5 presents 2 gas chromatograms of the dioxane-DDT solutions used in these studies. Tracing B represents the solution used for p,p'DDT diffusion studies in which the radioisotope was p,p'DDT (maximum purity available). The other components o,p'DDT and p,p'DDE, although present, were not tagged.

Additional experiments were performed later using solution A which was derived from B. Note the decrease in p,p'DDT and significant increases in unknown decomposition products. The diffusion coefficients for these materials are presented in Table II.

Table II - Apparent diffusion coefficients for decomposition products of p,p'DDT in dioxane water mixtures for 2 levels of added DDT.

Percent Dioxane	Percent Water	Diffusion coefficient D $cm^2/sec.$
	50 ppm added DDT	
100	0	2.2×10^{-6}
30	70	0.6×10^{-6}
28	72	0.5×10^{-6}
24	76	0.3×10^{-6}
	10 ppm added DDT	
100	0	2.2×10^{-6}
21	79	0.3×10^{-6}
14	86	0.3×10^{-6}

In comparison to the previous table, the D in 100 percent dioxane is the same order of magnitude as for p,p'DDT. However, the decomposition products appear to be much more soluble in water since the D does not decrease to the same degree as the water content increases.

From these studies on the diffusion of p,p'DDT it can be concluded that the solubility of DDT in water will limit its distribution in soil and water systems if the only means of transport is by molecular diffusion. Even though the solid phase may not adsorb appreciable quantities of DDT the immiscible nature of p,p'DDT in water will limit its movement in soil.

However, if an agent is present to render the p,p'DDT form soluble or miscible with water, then the diffusion processes must be considered. Also, if the para para form decomposes to more soluble forms such as o,p'DDT, DDE and other decomposition products, then the disappearance of the para form from the system may take place by diffusion (Section II).

4.5 Literature Cited

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4.6 Figures

Figure 1. Experimental and theoretical distribution of p,p'DDT (Cl^{36} DDT vs. DDT) in Na kaolinite clay at 100% dioxane and 25°C.

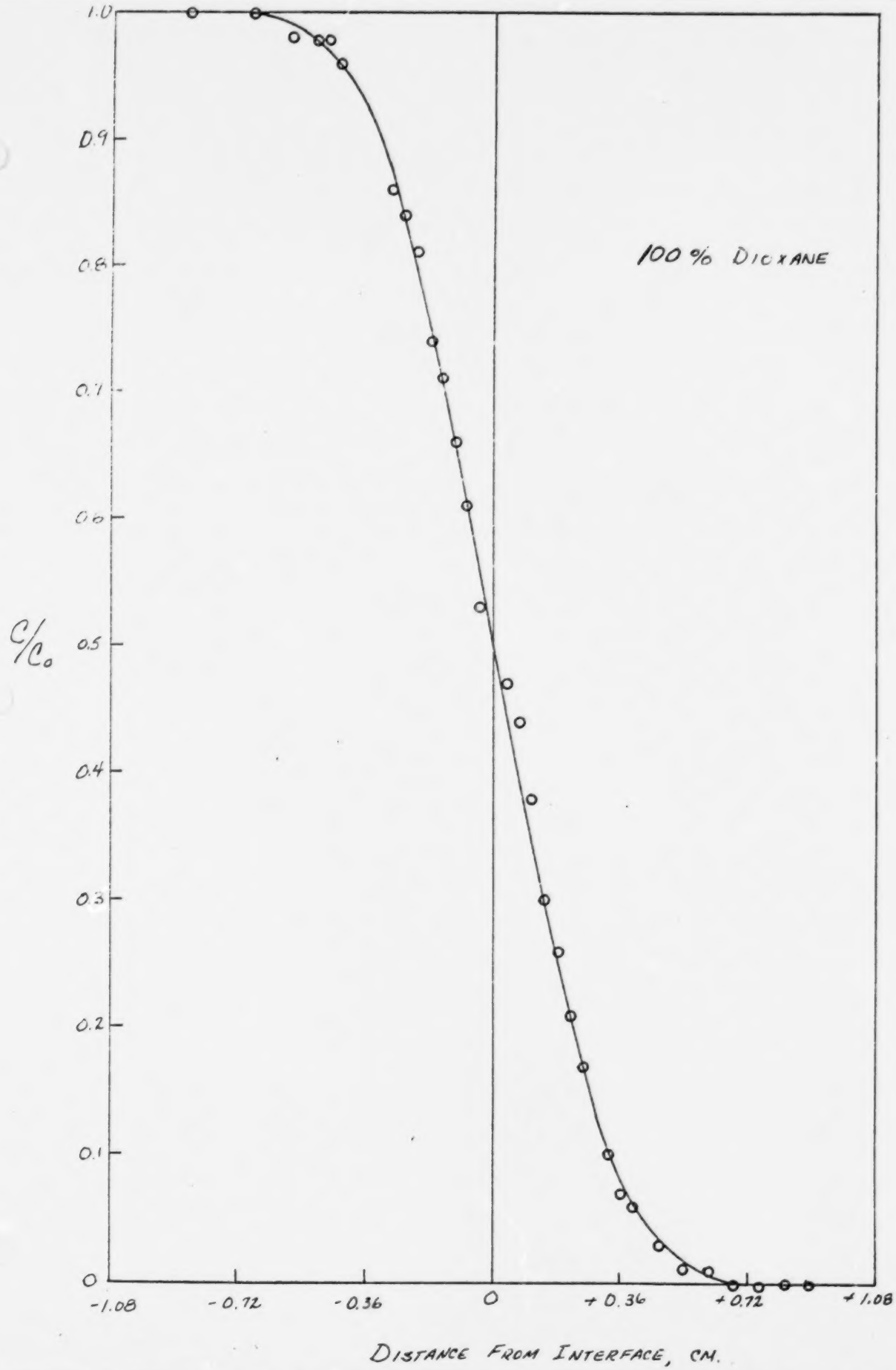

100 % DIOXANE
C/C₀
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-1.08
-0.72
-0.36
0
+0.36
+0.72
+1.08
DISTANCE FROM INTERFACE, CM.

Figure 2. Experimental and theoretical distribution of p,p'DDT (Cl^{36}DDT vs. DDT) in Na kaolinite clay at 75% dioxane and 25% water at 25°C.

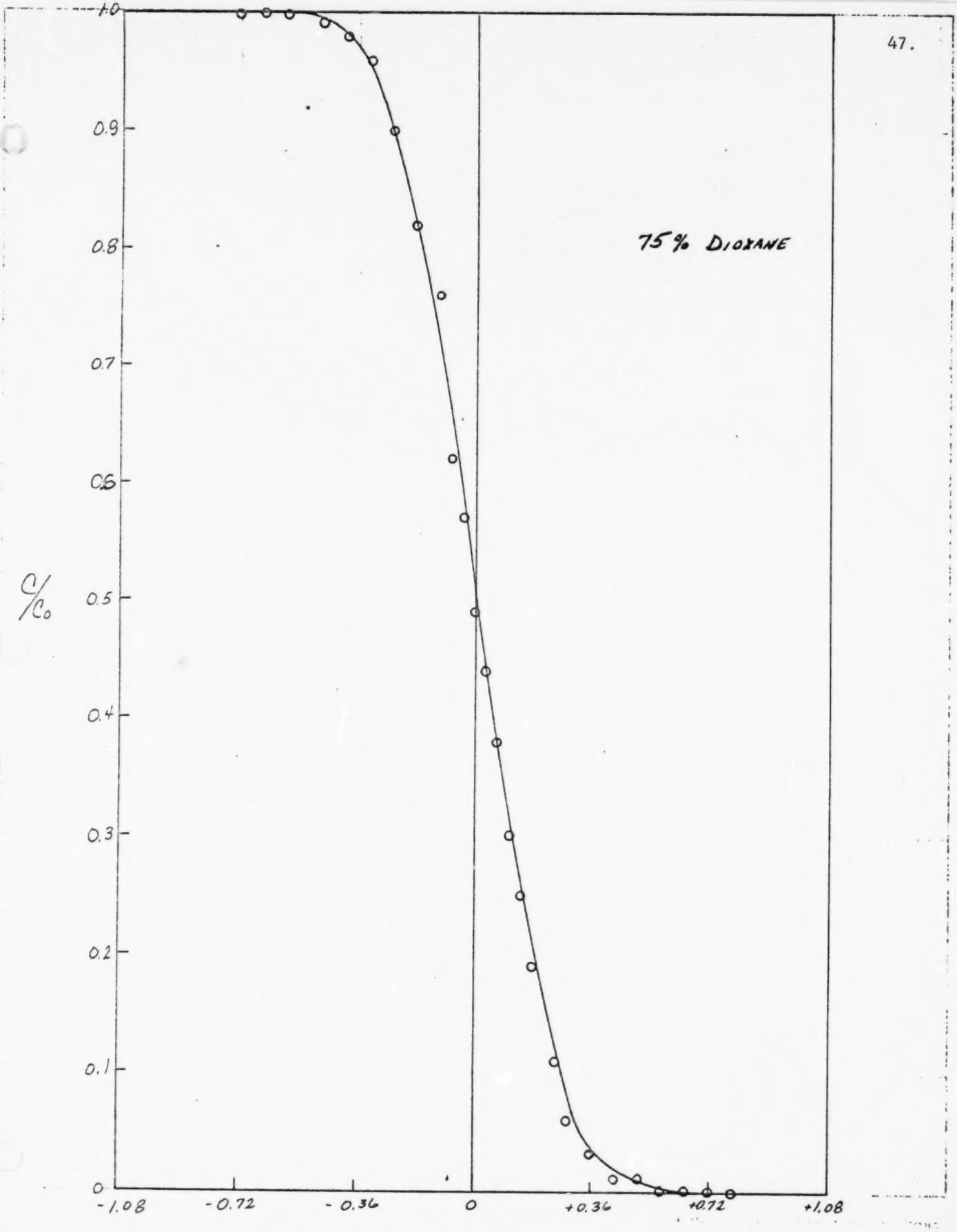

75% DIOXANE
C/C0
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-1.08
-0.72
-0.36
0
+0.36
+0.72
+1.08
DISTANCE FROM INTERFACE, Cal. CM

Figure 3. Experimental and theoretical distribution of p,p'DDT (Cl^{36}DDT vs. DDT) in Na kaolinite clay at 50% dioxane and 50% water at 25°C.

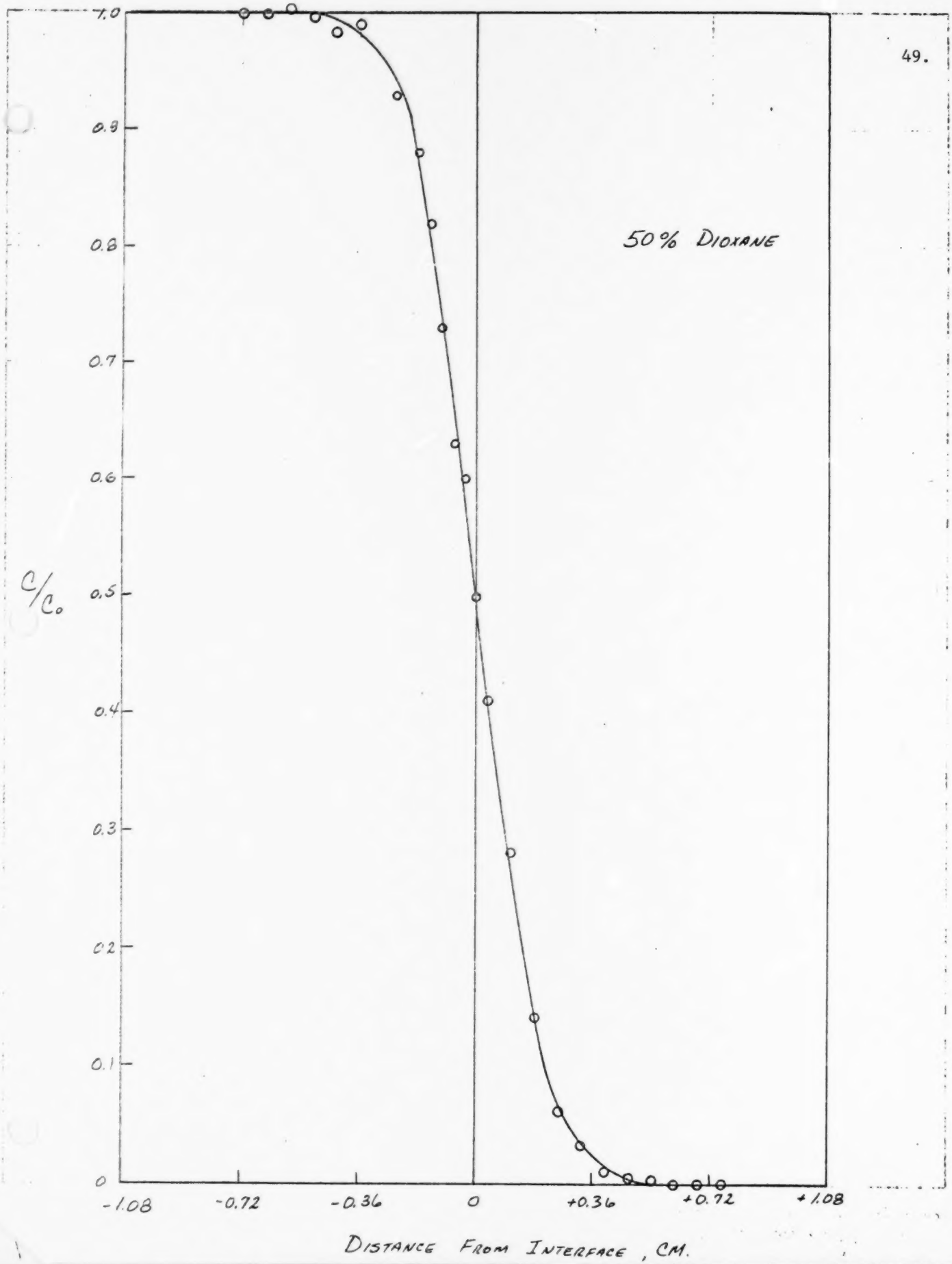

50% Dioxane
C/C₀
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-1.08
-0.72
-0.36
0
+0.36
+0.72
+1.08
Distance From Interface, CM.

Figure 4. Experimental and theoretical distribution of p,p'DDT (Cl^{36}DDT vs. DDT) in Na kaolinite clay at 25% dioxane and 75% water at 25°C.

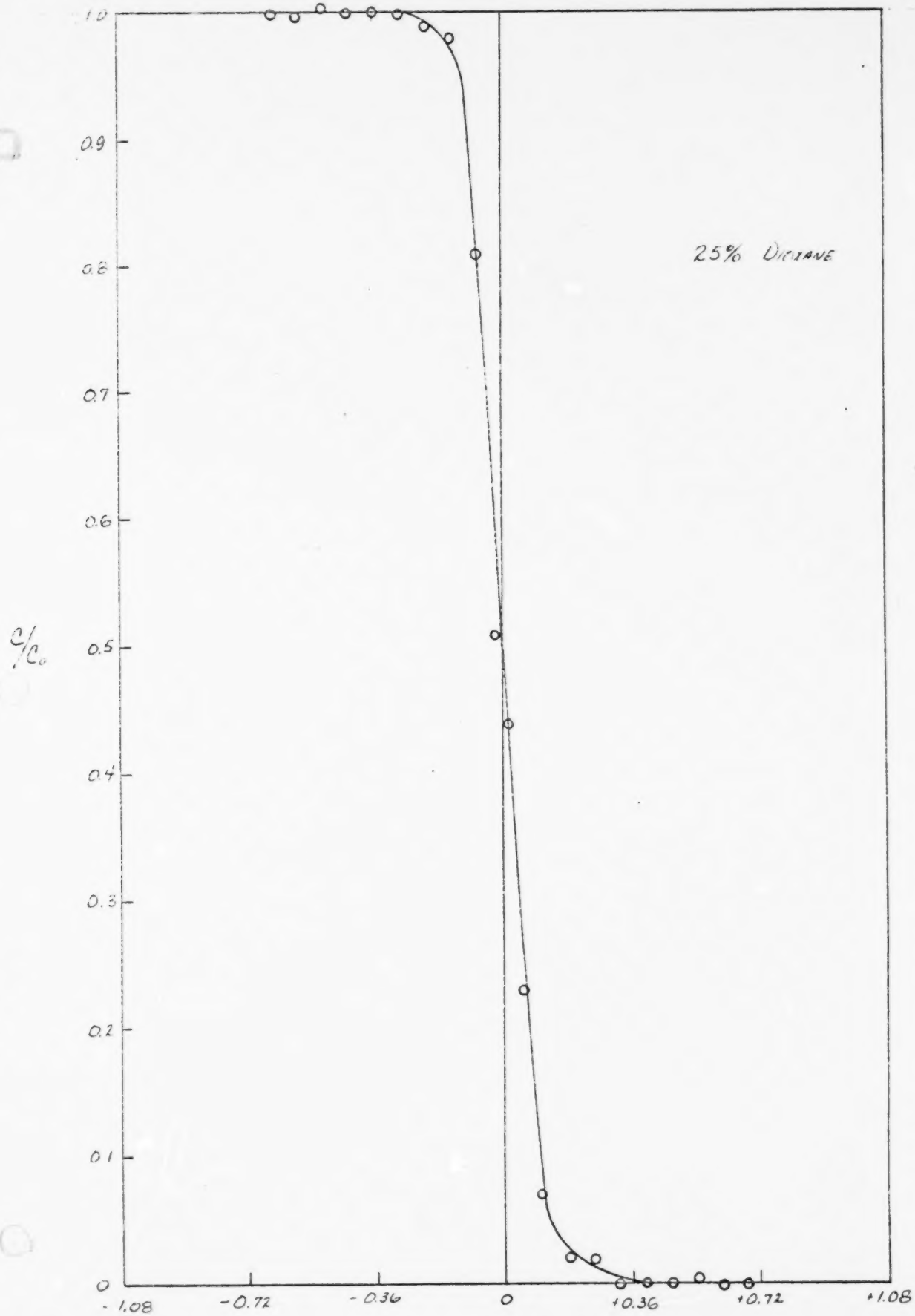
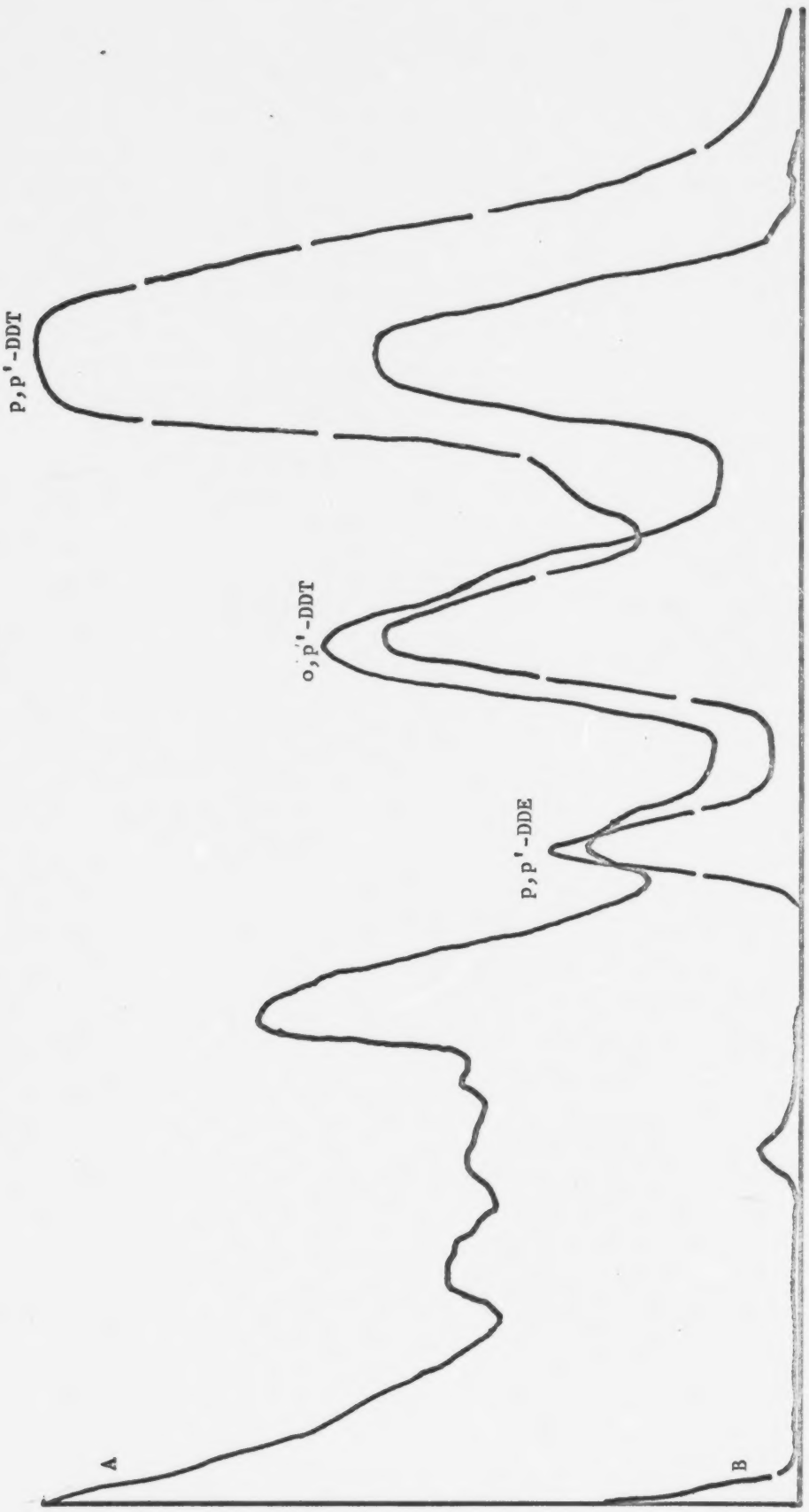

25% Distance
C/Co
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-1.08
-0.72
-0.36
0
+0.36
+0.72
+1.08
Distance From Interface, Cm.

Figure 5. Gas chromatography tracing of fresh Cl^{36} DDT dioxane solution (cuve B) and Cl^{36} DDT solution in dioxane after decomposition of p,p'DDT (curve A).


p,p'-DDT
o,p'-DDT
p,p'-DDE
A
B

SECTION IV. Miscible and Immiscible Displacement of DDT Solutions in Columns of Soil

5.1 Introduction

The extent of movement of a pesticide through the soil will depend upon its solubility in water, the extent of adsorption by the solid, the rate and quantity of flow of water and the diffusion characteristics of the pesticide. Some estimates concerning the extent of these processes can be obtained by studying movement in columns. This method has the advantage of integrating all processes but the disadvantage of not allowing evaluation of the magnitude of the contribution of individual processes. For this reason these various processes are studied separately while at the same time the interaction of these processes can be ascertained only by actual flow experiments.

The rate equations of Thomas (4) and Hiester and Vermeulen (2), Opler and Hiester (3) can be used to analyze and predict (providing they predict the experimental data) the extent of movement for experimentally undetermined conditions. Symbols are defined in the accompanying Table I.

5.2 Theory

Two equations govern the behavior of the adsorbate as it moves through the adsorbent column. The mass conservation equation expresses the fact that in any infinitesimal volume of soil a loss of adsorbate (DDT) from the solution following through that volume must equal the gain of that adsorbate, adsorbed on the soil and contained in the soil voids:

$$-\left(\frac{\partial C_A}{\partial z}\right)_v = \rho\left(\frac{\partial q_A}{\partial v}\right)_z + f\left(\frac{\partial C_A}{\partial v}\right)_z$$

where v is the volume, ρ the bulk density and z the depth. The second equation is that governing the rate of adsorption at the solid surface. For the system

$$A + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A \cdot X$$

where A is DDT in solution and X is the adsorbent

$$\frac{d(A \cdot X)}{dt} = k_1 (A) (X)$$

$$= k_2 (A \cdot X)$$

If $A = C_A$ and $A \cdot X = q_A$ and $X = Q - q_A$ the rate equation becomes

$$\frac{dq_A}{dt} = k_1 C_A (Q - q_A) - k_2 q_A$$

where k_1, k_2, are rate constants, q_A adsorbed DDT and Q the total adsorption capacity, t the time.

To express the equilibrium relationship between the adsorbed and solution DDT it was found in Section V on adsorption that the Langmuir equation provides an approximation which may be used in the column studies.

As applied to DDT adsorption we may write

$$q_A = \frac{(K Q C_A)}{(1 + K C_A)}$$

where K is the adsorption equilibrium constant, Q the total adsorption capacity, and C_A concentration of DDT in solution. When C_A/q_A is plotted against C_A, a linear isotherm is obtained. The constant K is obtained by dividing the slope of the isotherm by its intercept while the capacity Q is the reciprocal of the slope of the isotherm.

Hiester and Vermeulen (1) and Opler and Hiester (2) have published numerical and graphic solutions of their equations in terms of the parameters r, s, t, λ, and w. Details on the derivations and solutions are available in the above publications. The five parameters are:

$$r = \frac{1 + K\,(C_A)_o^*}{1 + K\,(C_A)_o}$$

$$s = \frac{kQ\rho}{1 + K\,(C_A)_o^*} \quad \frac{z}{R}$$

$$t = \frac{k\,(1 + K\,(C_B)_o)}{K} \quad \frac{V - zf}{R}$$

$$\lambda = \frac{C_A - (C_A)_o^*}{(C_A)_o - (C_A)_o^*}$$

$$w = \frac{q_A - (q_A)_o}{(q_A)_o^* - (q_A)_o}$$

A comparison between theory and experiment can be made in the following way. λ and the ratio t/s for each sample of effluent is calculated. Average values of V are calculated by averaging cumulative volumes of effluent at the start and end of the interval of collection. λ is then plotted versus t/s and compared with theory. For the experimental conditions being employed, the parameter s for a given column is constant while t is a function of the volume of effluent. The ratio t/s is calculable without a knowledge of k the rate constant. Since the values of k are dependent upon specific properties of the column and are not directly measurable, s is not readily calculated. Values of s can be obtained by fitting experimental results at one value of λ versus t/s. Having obtained s, k can be calculated by rearrangement of the s parameter equation.

5.3 Experimental

An apparatus was specially designed (1) such that stationary flow conditions and water content of the media could be maintained when tracer-free water was replaced by water containing a dissolved tracer. It was desired that no mixing of the two waters occurred initially at the boundary between them. At the same time the contribution of flow

associated with the boundary between soil and soil container had to be eliminated. Also, samples of effluent to be analyzed for tracer concentrations had to be collected without disturbing stationary flow conditions. A cross-sectional sketch of the apparatus is given in figure 1. Samples of air-dry soil screened through a 2-mm. sieve were uniformly packed in the 30-cm. long lucite tubes. The water content and the flux density were controlled using hanging water columns and negative air pressure imposed on fritted glass bead porous plates shown on each end of the horizontal column. The use of fritted glass bead plates offers the advantage over other porous materials of having a negligible exchange capacity, large capillary conductivity and an exceedingly narrow pore size distribution.

The water in the small reservoir behind the inflow plate could be rapidly changed from one containing a tracer to tracer-free water or the reverse by the use of leveling bottles. Burettes graduated to 0.2 ml. were connected in the system to measure the volumes of water which entered the column. The X's in the figure are necessary on-off valves. The vacuum arrangement allowed samples of effluent to be collected as close as possible to the end of the soil column thereby eliminating further dispersion of solutes outside the sample. During the time samples were not being collected, water flow was maintained by means of suction obtained from hanging water columns at the same suction as the vacuum arrangement. The necessary valves for this operation are indicated on the effluent side of the soil column.

The soil moisture suction over the entire length of column was almost the same value even though small differences in suction were required for flow. At the greatest average suctions used, the difference in suctions at the ends of the column never exceeded 5 cm. water. All studies were made under controlled temperature conditions.

Oakley sand was the soil investigated. Non-tracer water was 0.01N $CaSO_4$ or a mixture of 50:50 alcohol:water as noted in results. Miscible displacements of DDT (tracer) and DDT free water (non-tracer) were made at different flow velocities (1.10 and 0.61 cm per hr) and water contents.

5.4 Results and Discussion

The breakthrough curves of C/C_o vs pore volume of effluent p,p'-DDT movement in Oakley sand are presented in figures 2, 3, 4, and 5. In figure 2, a mixture of 50:50 alcohol:water containing 50 ppm of DDT displaced a 0.01N solution of $CaSO_4$ at a flux of 1.1 cm/hr. It is evident that the adsorption capacity of the soil, having an exchange capacity of 3.0 me. per 100 gm. is rapidly satisfied at this high concentration of DDT. The breakthrough curve is extremely uniform and should be amenable to the mathematical analysis previously outlined.

Figure 3 is the elution of the DDT from the same column as presented in figure 2. Calcium sulfate water is displacing the alcohol water mixture and the abruptness of the elution is evidence that the process does not include the removal of adsorbed DDT. The displacement and mixing of the resident solution with the displacing solution is the main reaction.

In contrast to figures 2 and 3, figures 4 and 5 represent the addition of DDT to a column of Oakley sand and the elution of the pesticide at a lower flux (v). Here the solvent is again 50:50 alcohol:water displacing $CaSO_4$ but the elution is by alcohol water mixture free of DDT.

The desorption of DDT into the elution solution is quite similar to the breakthrough curve. This indicates that the desorption is similar to adsorption providing the solvent will dissolve or remove the DDT adsorbed. However, by contrast, the previous elution was by water in which the solubility of DDT is very low. In this case the elution curve approaches $C/C_o = 0$ even though considerable DDT remains adsorbed and trapped in the soil surface.

Adsorption batch studies of DDT on this soil have been difficult because of the low adsorption capacity and the difficulties of analysis. New methods have been developed to obtain adsorption isotherms in order to test the H-V theory. In addition, breakthrough and elution curves for lower concentrations of DDT and mixed solvents approaching water

without alcohol are now being measured. Solutions of commercial DDT are also under experimentation to compare with the more chemically pure systems involving p,p'-DDT.

It may be tentatively concluded that the application of DDT in water emulsions may penetrate soil and remain mobile only to the extent that the emulsifier is present. The DDT having once been deposited will not be readily leached. This is true not because of the high bonding energy between soil and DDT but rather because of the low solubility of DDT in water.

Table I

List of Symbols

C_A = concentration of DDT in the solution phase at some depth (mg/ml)

$(C_A)_o$ = concentration of DDT in solution in the influent (mg/ml)

$(C_A)_o^*$ = initial concentration of DDT in the solution phase coexisting with $(q_A)_o$ in the adsorbed phase (mg/ml)

q_A = concentration of DDT in the adsorbed phase in the column (mg/gm)

$(q_A)_o$ = concentration of DDT initially present in the adsorbed phase (elution) (mg/gm)

$(q_A)_o^*$ = concentration of DDT in the adsorbed phase in equilibrium with the coexisting concentration of $(C_B)_o$ in solution (mg/gm)

Q = total adsorptive capacity (mg/gm) (1/slope of Langmuir isotherm)

R = volumetric flow rate (ml/min/cm^2)

f = ratio of void space occupied by solution to total volume of column

k = adsorption rate constant (ml/mg/min)

K = adsorption equilibrium constant (ml/mg) (slope/intercept - Langmuir isotherm)

r = equilibrium parameters

s = column capacity parameter

t = solution capacity parameters

Table I (continued)

V = volume of solutions applied to the column (ml/cm^2)

z = depth of soil (cm)

λ = concentration ratio parameters for solution

ρ = dry bulk density (gm/cm^3)

w = concentration ratio parameter for the adsorbed phase

5.5 Literature Cited

1. Biggar, J. W. and D. R. Nielsen. Miscible displacement in porous materials. J. Soil Sci. 12:188-197, 1961.

2. Hiester, N. K. and T. Vermeulen. Saturation performance of ion-exchange and adsorption columns. Chem. Eng. Progress. 48:505-516, 1952.

3. Opler, A. and N. K. Hiester. Tables for predicting the performance of fixed bed ion exchange and similar mass transfer processes. Stanford Research Institute, Stanford, California.

4. Thomas, H. C. Heterogeneous ion exchange in a flowing system. J. Amer. Chem. Soc.66:1664-1666, 1944.

5.6 Figures

Figure 1: Schematic cross-section of apparatus used for collecting samples of effluent from soil columns maintained at constant water content and average flow velocity.

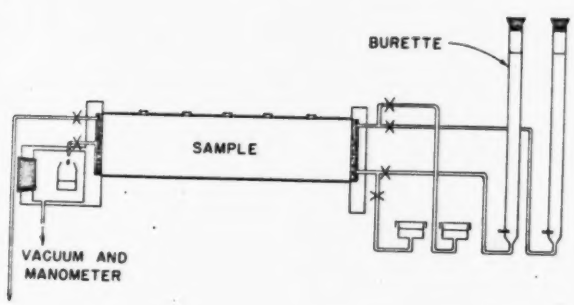

BURETTE
SAMPLE
VACUUM AND
MANOMETER

Figure 2: A breakthrough curve of a 50:50 mixture of alcohol-water containing 50 ppm p,p'-DDT displacing $CaSO_4$ solution at 1.1 cm/hr from Oakley sand.

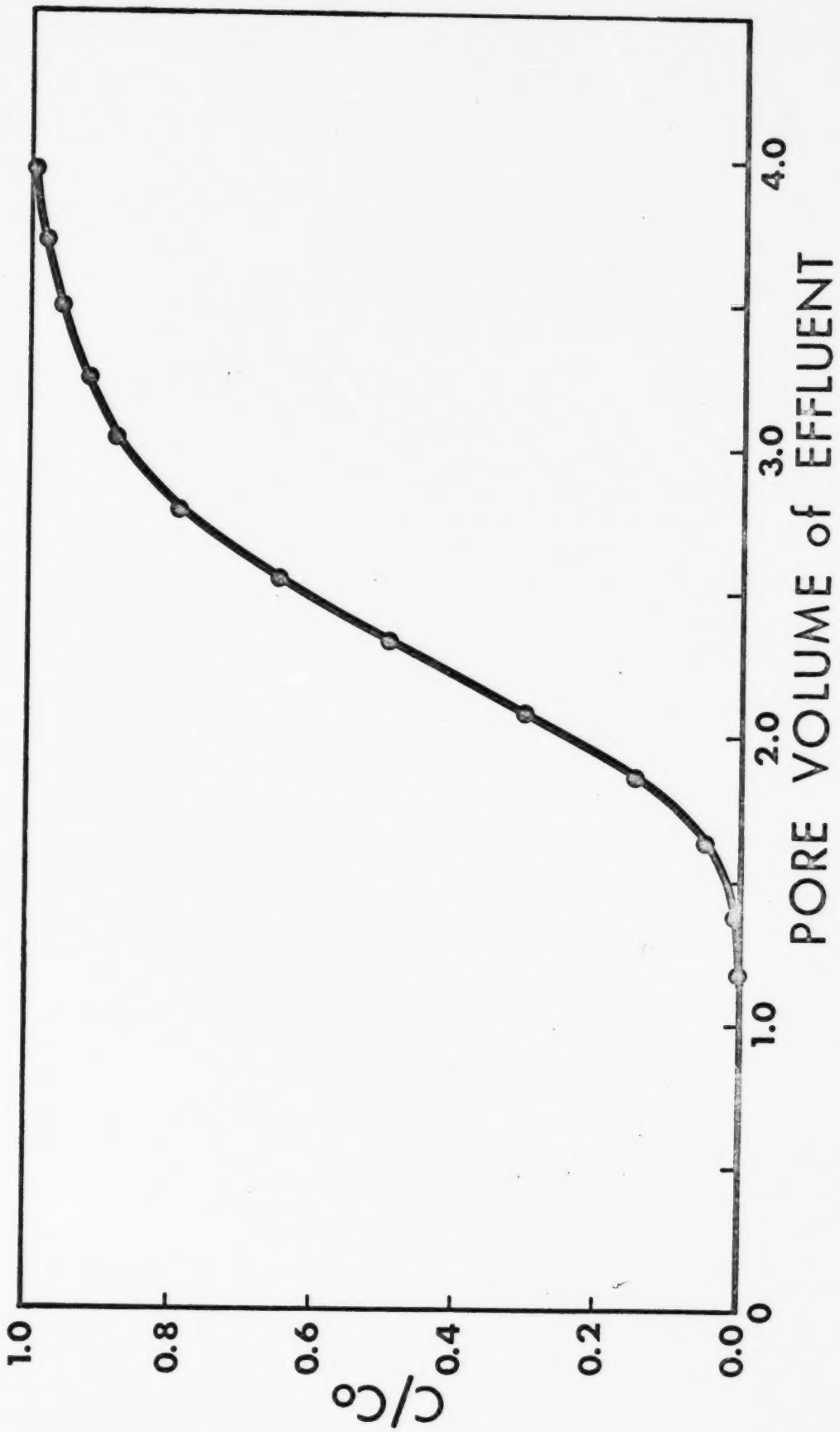

1.0
0.8
0.6
0.4
0.2
0.0
C/Co
0
1.0
2.0
3.0
4.0
PORE VOLUME of EFFLUENT

Figure 3: An elution curve of $CaSO_4$ displacing alcohol:water mixture containing 50 ppm DDT at 1.10 cm/hr from Oakley sand.

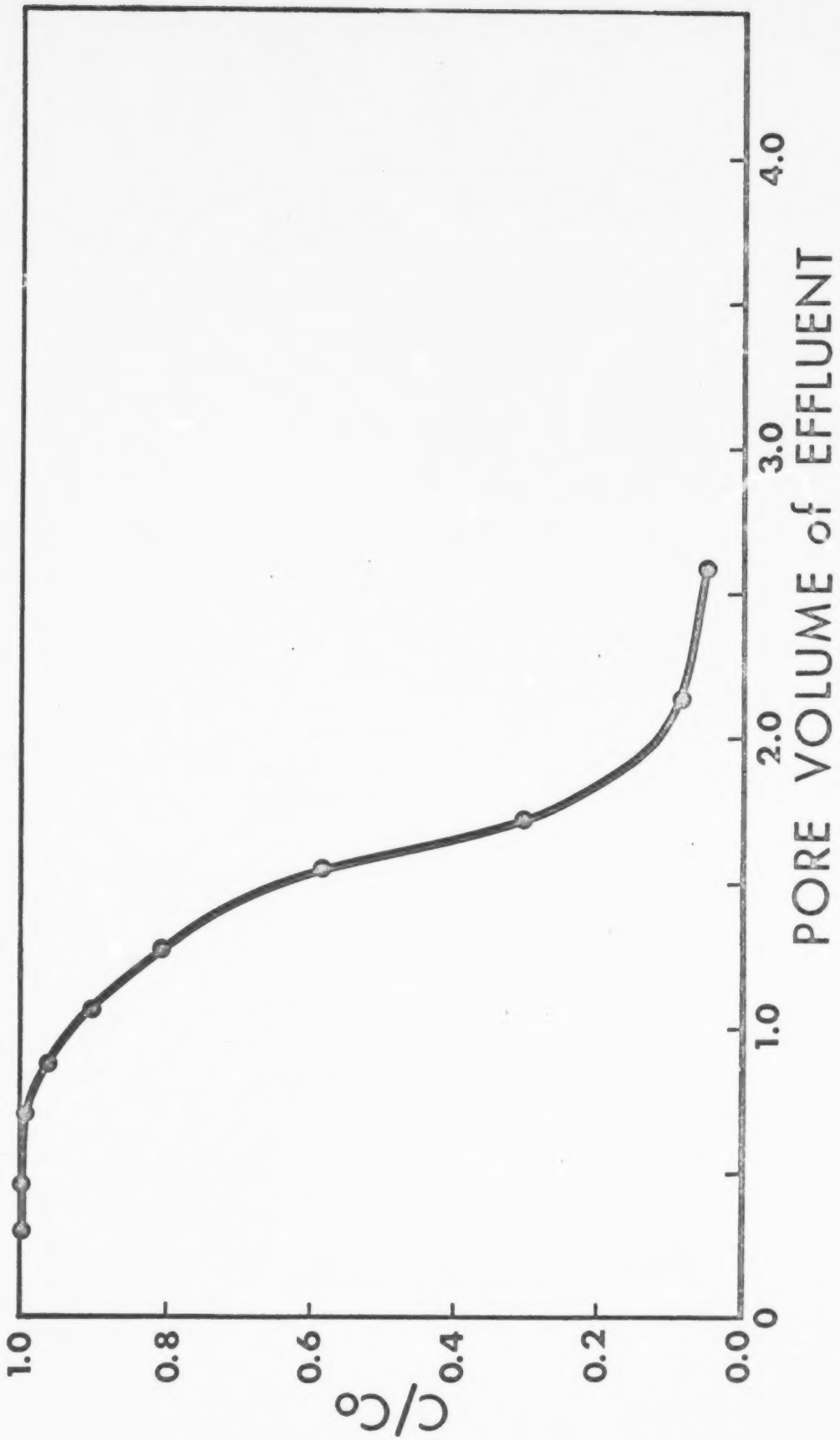

C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
1.0
2.0
3.0
4.0
PORE VOLUME of EFFLUENT

Figure 4: A breakthrough curve of a 50:50 alcohol:water mixture containing 50 ppm DDT displacing $CaSO_4$ at 0.61 cm/hr from Oakley sand.

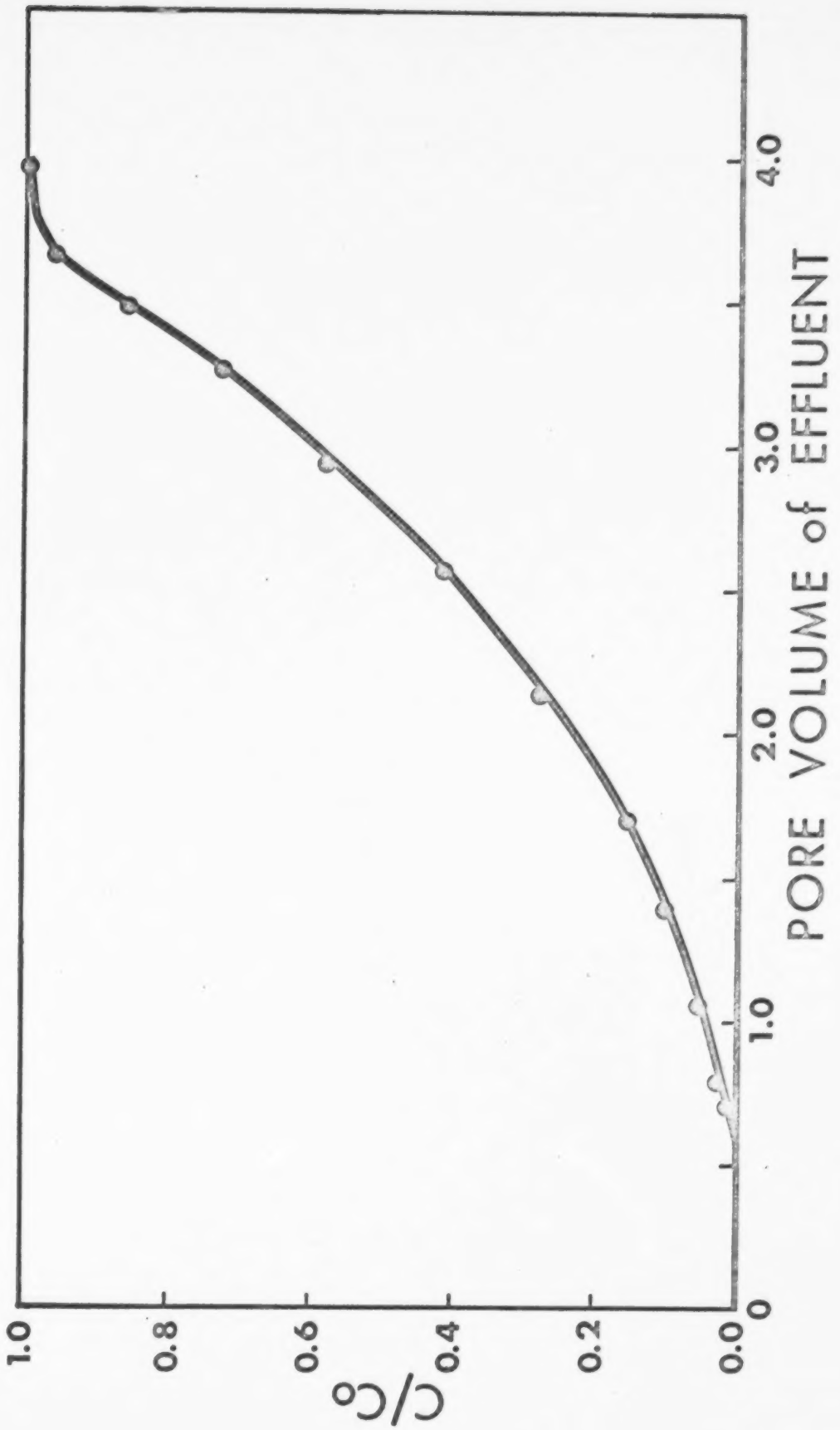
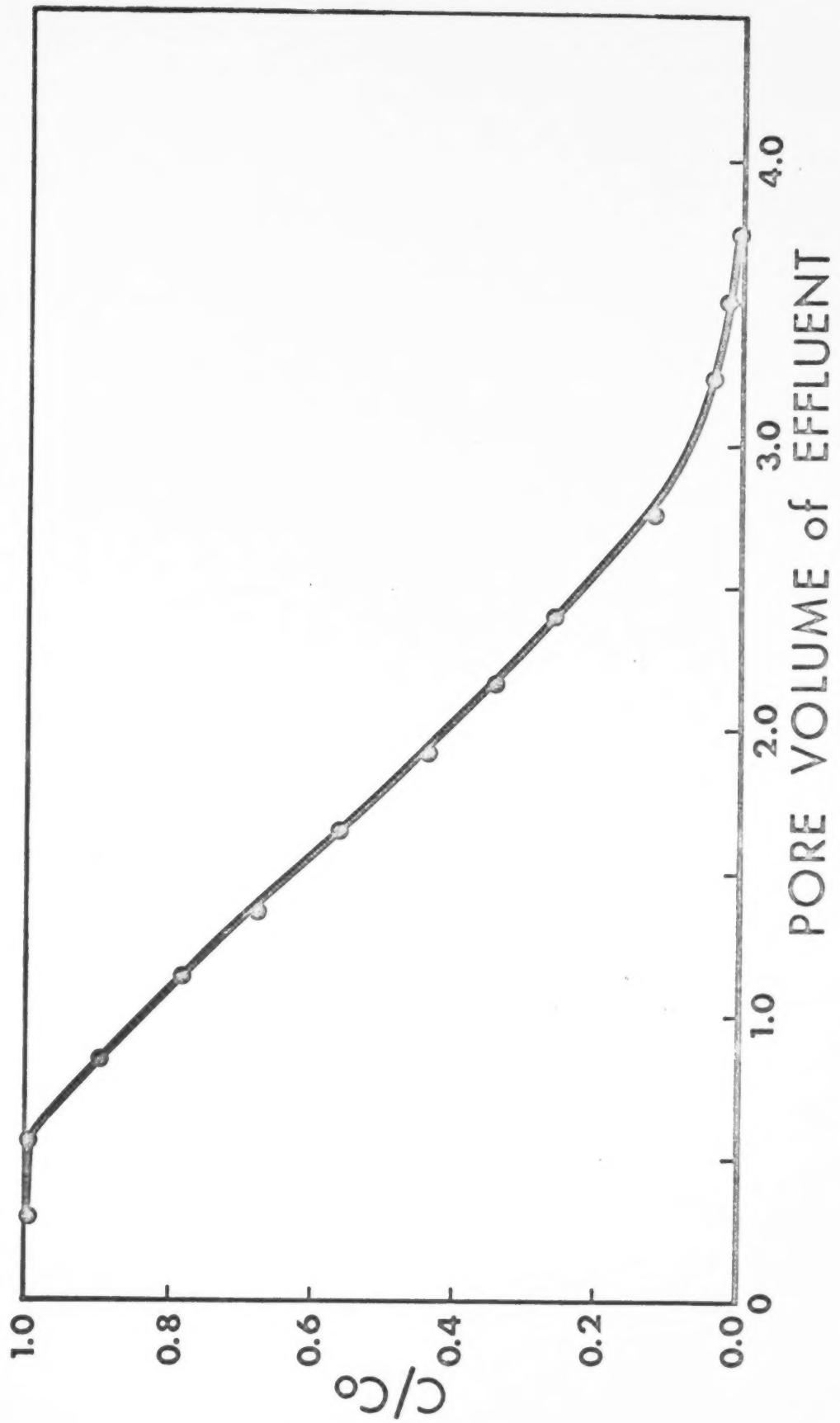

C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
1.0
2.0
3.0
4.0
PORE VOLUME of EFFLUENT

Figure 5: An elution curve corresponding to figure 4.


C/Co
1.0
0.8
0.6
0.4
0.2
0.0
0
1.0
2.0
3.0
4.0
PORE VOLUME of EFFLUENT

SECTION V. Adsorption of p,p'-DDT by Clays from Various Solvents

6.1 Methods and Results

Two percent suspensions of Na bentonite, Ca bentonite, raw bentonite, Na kaolinite and raw kaolinite were made using n-hexane, benzene, benzene:water 50:50 mixture, 95% ethyl alcohol, H_2O as solvents. To each of these suspensions p,p'-DDT was added at concentrations ranging from 25 ppm to 3000 ppm in some cases. The suspensions were shaken for 1 hour and 24 hours after which they were centrifuged and the supernatant liquid analyzed for DDT by gas chromatography.

The data for each treatment are presented in the accompanying tables. The data have been analyzed both by the Freundlich equation and the Langmuir equation. The former may be written as

$$\frac{x}{m} = K c \frac{1}{n}$$

where x/m is the quantity adsorbed and c is the equilibrium concentration. K is a constant characteristic of do media and usually has values between 1 and 5. The greater n is the more efficient is the adsorption at low concentrations.

The other equation, the Langmuir equation, has also been used to express the adsorption of constituents from solutions. This equation may be written

$$q_B = \frac{(K Q c_B)}{(1 + K c_B)}$$

where K is the adsorption equilibrium constant, Q the total adsorptive capacity and q_B, c_B the adsorbed and solution concentrations of DDT, respectively.

A plot of c_B/q_B versus c_B should yield a straight line.

The following observations may be made from the accompanying tables. At equal concentrations of added DDT, more DDT was taken up by bentonite than kaolinite. The greater surface area of the bentonite would partially account for this result. Whether bentonite or kaolinite was the adsorbent, more DDT was adsorbed from n-hexane than from benzene. This difference appears to be greater for the bentonite rather than the kaolinite system however. It did not seem to make any difference whether the cation was Na or Ca in that more was adsorbed from n-hexane than benzene.

It is interesting to note that more DDT was taken up by Ca bentonite than Na bentonite.

The uptake from alcohol was about the same for both Na bentonite and Ca bentonite. However, at equal concentrations of added DDT the uptake from benzene and hexane is much greater than from alcohol.

The adsorption of DDT from solvents involves several processes. The DDT molecule must be removed from solution, desorb the solvent from the surface and be adsorbed on the surface. The failure to compete successfully for a surface site will reduce the amount adsorbed. Hence in the case of both benzene and n-hexane, the DDT molecule although readily soluble in these solvents can successfully compete for surface sites. On the other hand, although the DDT is also readily soluble in alcohol, it cannot compete as successfully for surface sites against alcohol and thus is not as readily adsorbed. The alcohol having an OH group is more readily bonded than either benzene or hexane.

From these observations it may be concluded that soils containing the montmorillonitic type clays will adsorb more DDT than will soils containing kaolinite types.

An emulsifier can make the DDT more compatible with surface adsorbed water which is present under natural conditions. This will allow for greater uptake of DDT from solution, the DDT becoming trapped on the surface with the removal or decomposition of the

emulsifier. This is observed to some extent by comparing the benzene: H_2O mixtures and H_2O solutions with the alcohol solutions.

Calculation of the reaction energies is not deemed feasible until more accurate methods have been worked out to treat and analyze samples. Since temperatures have such a significant effect on the solubility (see Section II), it will probably affect the adsorption although to a lesser degree.

The Langmuir and Freundlich equations will be used in conjunction with flow experiments to estimate the adsorption-desorption during flow and relate the concentration in solution to that adsorbed.

Table I. Adsorption of p,p'-DDT from benzene by a 2 percent suspension of Ca bentonite at 25°C

Added DDT mg/ml	Adsorbed (1 hr.) mg/gm	Equil. Conc.[1/] mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc.[1/] mg/ml
10	0.20	6.0	0.25	5.0
25	0.35	18.0	0.50	15.0
50	1.40	21.0	1.65	17.0
100	2.10	58.0	2.40	52.0
250	2.60	198.0	2.90	192.0
500	2.90	442.0	3.25	435.0
1000	3.20	936.0	3.75	925.0
2000	4.80	1904.0	5.25	1895.0
3000	5.90	2882.0	6.65	2867.0

[1/] Equilibrium Concentration.

Table II. Adsorption of p,p'-DDT from n-hexane by a 2 percent suspension of Ca bentonite at 25°C

Added DDT mg/ml	Adsorbed (1 hr.) mg/gm	Equil. Conc. mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
10	0.20	6.0	0.25	5.0
25	0.40	17.0	0.55	14.0
100	2.45	51.0	2.75	45.0
250	2.90	192.0	3.20	186.0
500	3.20	436.0	3.60	428.0
1000	3.60	928.0	4.00	920.0
2000	5.30	1894.0	5.75	1885.0
3000	6.70	2866.0	7.50	2850.0

Table III. Adsorption of p,p'-DDT from 95 percent ethylalcohol by Ca bentonite at 25°C

Added DDT mg/ml	Adsorbed (24 hr.) mg/gm	Equiv. Conc. mg/ml
25	70	23.6
50	95	48.1
100	140	98.0
250	260	246.7
500	350	493.0
1000	450	991.0

Table IV. Adsorption of p,p'-DDT from a 50:50 benzene:H_2O mixture by a 2 percent Ca bentonite suspension

Added DDT mg/ml	Adsorbed mg/gm	Equiv. Conc. mg/ml
25	10.0	24.8
50	15.0	49.7
100	20.0	99.6
250	20.0	249.6
500	25.0	499.5
1000	45.0	999.0

Table V. Adsorption of p,p'-DDT from a water mixture by Ca bentonite at 25°C

Added DDT mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
25	10.0	24.8
50	10.0	49.9
100	10.0	99.8
250	15.0	249.6
500	20.0	499.5
1000	30.0	999.0

Table VI. Adsorption of p,p'-DDT from benzene by Na bentonite at 25°C

Added DDT mg/ml	Adsorbed (1 hr.) mg/gm	Equiv. Conc. mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
10	0.20	6.0	0.25	5.0
25	0.35	18.0	0.56	13.8
50	1.00	30.0	1.20	26.0
100	1.50	70.0	1.75	65.0
250	2.10	208.0	2.40	201.0
500	2.45	451.0	2.90	442.0
750	3.00	690.0	3.35	683.0
1000	3.20	936.0	3.60	928.0
2000	4.60	1908.0	5.25	1895.0
3000	6.45	2870.0	7.00	2860.0

Table VII. Adsorption of p,p'-DDT from n-hexane solution by Na bentonite 2 percent suspension at 25°C

Added DDT mg/ml	Adsorbed (1 hr.) mg/gm	Equil. Conc. mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
10	0.20	6.0	0.30	4.0
25	0.40	17.0	0.55	14.0
50	1.20	26.0	1.40	22.0
100	1.75	65.0	2.15	57.0
250	2.45	200.0	2.80	194.0
500	2.85	445.0	3.25	435.0
750	3.40	682.0	3.75	675.0
1000	3.75	925.0	4.25	915.0
2000	5.30	1894.0	6.00	1880.0
3000	7.10	2854.0	7.60	2848.0

Table VIII. Adsorption of p,p'-DDT from 95 percent ethyl-alcohol by Na bentonite at 25°C

Added DDT mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
25	70	23.6
50	100	48.0
100	150	97.0
250	275	244.5
500	325	493.5
750	-	742.4
1000	460	990.6

Table IX. Adsorption of p,p'-DDT from 50:50 benzene:H_2O mixture by Na bentonite at 25°C

Added DDT mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
25	10	24.8
50	15	49.7
100	20	99.6
250	25	249.5
500	30	499.4
1000	50	999.0

Table X. Adsorption of p,p'-DDT from water by Na bentonite 2 percent suspension at 25°C

Added DDT mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
25	10	24.8
50	10	49.9
100	10	99.8
250	15	249.6
500	20	499.5
1000	30	999.1

Table XI. Adsorption of p,p'-DDT from n-hexane by Na kaolinite at 25°C and 24 hours

Added DDT mg/ml	Adsorbed (24 hrs.) mg/gm	Equiv. Conc. mg/ml
25	0.10	22.6
50	0.15	47.0
100	0.25	94.5
250	0.35	243.0
500	0.50	488.0
1000	0.80	984.0
2000	1.45	1971.0

Table XII. Adsorption of p,p'-DDT from benzene by a 2 percent suspension of Na bentonite at 25°C

Added DDT mg/ml	Adsorbed mg/gm	Equiv. Conc. mg/ml
25	0.10	22.5
50	0.15	47.0
100	0.20	95.8
250	0.30	244.0
500	0.50	488.0
1000	0.70	986.0
2000	1.40	1972.0

SECTION VI. Publications

R. R. Riggs and J. W. Biggar. Ultrasonic suspension of chlorinated pesticides in aqueous media. Soil Sci. Soc. Amer. Proc. 29:629, 1965.

J. W. Biggar and D. R. Nielsen. Miscible displacement and leaching phenomenon. Accepted for publication - American Society of Agronomy Monograph on Irrigation.

J. W. Biggar, G. R. Dutt, and R. R. Riggs. Solubility of p,p'-DDT in water by gas chromatography. Submitted for publication - J. Food and Agr. Chem.

J. W. Biggar, R. K. Jackson, and A. G. Hornsby. Self diffusion of p,p'-DDT in Clay-Dioxane and water systems. Report to the California Agricultural Experiment Station #2, 1964-65 (paper in review).

J. W. Biggar and R. R. Riggs. Adsorption of p,p'-DDT from Benzene, Hexane and Alcohol-water solutions by clay. Report to the California Agricultural Experiment Station #1, 1962-63, No. 3, 1964-65. (paper in preparation)

J. W. Biggar and R. R. Riggs. Solubility-temperature interactions for chlorinated hydrocarbons in water. Report to Western Regional Research Committee, October 1965. (paper in preparation)

SECTION VII. Appendix

8.1 Preparation of Clays

A. Prepare a 2% suspension of bentonite in H_2O.

($\cong$ 900 g to 40 l H_2O)

B. Clay suspension stirred 1 hour, allowed to stand overnight, stirred again for 1 hour. Allowed to settle until all particles > 1μ have settled (27:20 hr. to a depth of 35 cm.).

C. > 1μ fraction discarded.

D. 1μ + < 1μ fraction stirred for 1 hour and allowed to settle until all particles between 0.2μ and 1μ have settled. (526 hr. to a depth of 27 cm.)

E. < 0.2μ fraction siphoned off and discarded.

F. Steps D and E repeated once.

G. 0.2μ to 1μ fraction suspended in 40 l of 1N NaCl sol. and stirred for 1 hr. Na-bentonite allowed to settle. Supernatant siphoned off and discarded.

H. Step G repeated 3 times.

I. Following the Na treatment, the clay is washed 7 to 8 times with 40-45 l of H_2O each time and stirred 1 hr. The Na-clay settled readily the first 4-5 washings. The later washings are settled by centrifugation at 17000 rpm and 23°C using a Model KSB-R Servall continuous flow centrifuge. The effluent is tested with $\cong$ 0.1N No_3 sol. until a negative test for chloride is observed.

J. The chloride free Na-bentonite is collected from the centrifuge tubes and lyophilized in wide-mouth flasks at a minimum of 10^{-3} mm Hg. (should hold 10^{-4} and probably is better than that.) Sample flasks held at room temperature.

Note: Other clays prepared as Na except Ca salts replace Na salts; Kaolinite, bentonite, illite.